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ERRATA.

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PART I.

Page	Line	
266	19*	for " <i>diethylaminethyl</i> " read " <i>diethylaminopropyl</i> ."
275	8*	„ " <i>2-Phenylpyrrolidine</i> " read " <i>2-Phenylpyrrolone</i> ."
288	13, 14	„ " <i>3-phenyl-1-methyl-2-quinoline</i> " read " <i>3-phenyl-1-methyl-2-qui-</i>

PART II.

421	11*	for " <i>J. Lander</i> ," read " <i>J. esper. Lander</i> ."
422	19*	„ " <i>one inch</i> " read " <i>nine inches</i> ."

VOL. XCIII (TRANS., 1908).

486	1*	for " $C_{12}H_{14}O_{14}N_6 \cdot 3H_2O$ " read " $C_{12}H_{14}O_{14}N_6Mn \cdot 3H_2O$."
189	5	„ " $C_{12}H_{14}O_{14}N_6$ " read " $C_{12}H_{14}O_{14}N_6Ni$."
912	3*	„ " $C_{28}H_{37}CO_2H$ " read " $C_{28}H_{37}CO_2H$."
1171	11*	„ " $C_6H_{10} \begin{smallmatrix} / \\ CO_2H \end{smallmatrix}$ " read " $C_6H_{10} \begin{smallmatrix} / \\ CO_2H \end{smallmatrix}$ "
1173	3	„ " <i>standard</i> " read " <i>silver</i> ."

* From bottom.

suspending the substance in dry ether and passing in dry hydrogen chloride, a *hydrochloride* was produced. This was crystallised from water, and the chlorine estimated by titration with standard sodium solution.

Found: Cl = 11.6, 11.3.

* $C_{14}H_{21}O_5N_2.HCl$ requires Cl = 11.0 per cent.

(2) Condensation with Aspartic Acid.

Molecular proportions or 5 grams of the amino-acid hydrochloride and 5 grams of aspartic acid were mixed together and heated with 30 c.c. absolute alcohol in a sealed tube at 110–120° for four hours. On cooling, a solution, after being filtered from some deposited aspartic acid, was allowed to evaporate. The crystals obtained were dissolved in water, neutralised with sodium hydroxide, and, on standing, colourless crystals were deposited.

Found: N = 7.6, 7.4.

$C_{26}H_{41}O_{10}N_4$ requires N = 7.58 per cent.

The condensation of one molecule of aspartic acid with two molecules of the amino-acid had thus taken place with elimination of two molecules of water.

The residue of unchanged aspartic acid is thus accounted for.

The substance gave a copper salt when a hot aqueous solution was added with a hot solution of copper acetate. On cooling, bluish-violet crystals were deposited.

Found: Cu = 10.34, 10.43.

$C_{16}H_{26}O_{10}N_2Cu$ requires Cu = 10.31 per cent.

Condensation of the amino-acid with benzaldehyde appeared to take place when the two substances were heated together, but the product was uncrystallisable. With anthranilic acid no change seemed to take place.

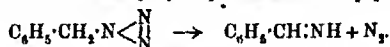
ROYAL COLLEGE OF SCIENCE, LONDON,
SOUTH KENSINGTON, S.W.

CXIV.—*The Triazo-group. Part IV. Allylazoim*

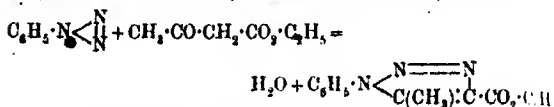
By MARTIN ONSLOW FORSTER and HANS EDUARD FIERZ.

ATTENTION has been directed at various times to the facility with which the atoms composing the triazo-group part company, as testified by the following illustrations.

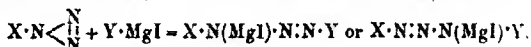
Benzylazoimide is resolved by acids into benzylideneimine nitrogen (Curtius and Darapsky, *J. pr. Chem.*, 1901, [ii], 63, 428).



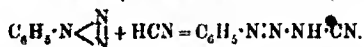
Phenylazoimide under the influence of sodium ethoxide may be condensed with numerous esters, yielding triazole derivatives (Dimroth, *Ber.*, 1902, 35, 1029, 4041; *Annalen*, 1904, 335, 1):



Alkyl- and arylazoimides are transformed into diazoamino compounds by the action of organo-magnesium derivatives (Dimroth, *Ber.*, 1903, 36, 909; 1905, 38, 670; 1906, 39, 3906):



Potassium cyanide converts phenylazoimide into benzene diazoamide (Wolff and Lindenhayn, *Ber.*, 1904, 37, 2374):

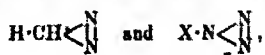


A trace of sodium ethoxide liberates two-thirds of the nitrogen from triazo-ketones (Forster and Fierz, *Trans.*, 1905, 87, 826; 1st vol., pp. 73 and 669):

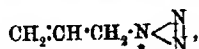


As an explanation of the last-named change, it has been suggested that, prior to elimination of nitrogen, the carbonyl group becomes saturated by the triazo-group, giving rise to an unstable cyclooid which forthwith collapses.

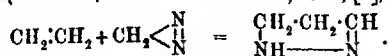
The foregoing considerations, coupled with certain points of resemblance between diazomethane and the triazo-group,



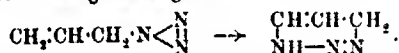
s to investigate the properties of allylazoimide, in which com-



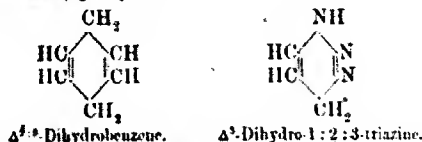
might anticipate the display of some attraction on the part of the iod linking for the highly active triazo-group; given a suitable comment, there should occur redistribution of affinities analogous to the interaction of ethylene and diazomethane, of which the outcome is shown in the case of diazoline (Azzarello, *Atti R. Accad. Lincei*, 1905, [v], 14, ii, 235):



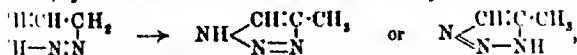
In attempting to prepare allylazoimide from sodium azide and allyl iodide or iodide, interaction took place with moderate readiness, but it was noticed that, unless quickly removed, the triazo-derivative undergoes a profound change, in consequence of which we have never obtained yields exceeding 30 per cent. This is explained by the fact that allylazoimide, a liquid which boils at 76.5°, changes slowly without external stimulus, into a crystalline, isomeric, diazoamino-compound, which melts at 192° and is very sensitive towards acids. Reflecting on the probable constitution of this compound, we were at first disposed to regard it as having a cycloïd structure arising from allylazoimide by the following rearrangement:



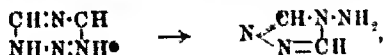
The ring would be called dihydrotriazine, and represents, so far as we have been able to ascertain, a new type of cycloïd; it is, in fact, a cyclohexene in which one-half of the molecule is replaced by the diazino(triazene)-group:



In drawing this conclusion, we have not overlooked the possibility of secondary transformation into the isomeric methyl-1:2:3-triazole,



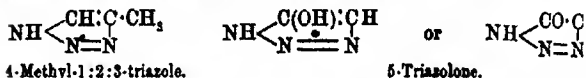
suggested by the recognition of the substance originally called di-tetrazine as 1-amino-3:4-triazole (Bülow, *Ber.*, 1906, 39, 8),



and of *N*-dihydro-tetrazinedicarboxylic acid (bis-diazoacetic acid 1-amino-3:4-triazole-2:5-dicarboxylic acid,

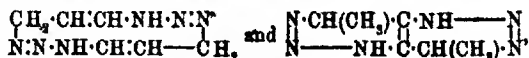


Our reason for preferring the hexacycloid representation is two. Although the uncertainty hitherto prevailing as regards the constitution of bis-diazoacetic derivatives has been removed by the agreement with Bülow's views on the part of Curtius, Darapsky, Müller (*Ber.*, 1907, 40, 1470), all doubt as to the possibility of a tetrazine ring existing has been removed since the recent isolation of 1:2:4:5-tetrazine, by the authors mentioned (*ibid.*, p. 84). In second place, if the crystalline isomeride of allylazoimide, 4-methyl-1:2:3-triazole, it might be expected to resemble the azolone described by Curtius and Thompson (*Ber.*, 1906, 39, 4) as arising from diazoacetamide by the action of baryta:



Nevertheless, the two substances are distinguished sharply by their behaviour towards very dilute acids, which forthwith liberate two thirds of the nitrogen from the compound under discussion, the recalling the most conspicuous property of the aliphatic diazoamides derivatives.

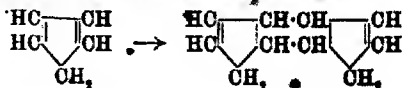
It has been mentioned that the transformed allylazoimide melts at 192°, a temperature which suggested a condition of polymerisation and the elevation of boiling point in chloroform agrees with the formula $(\text{C}_3\text{H}_5\text{N}_3)_x$. This observation might perhaps invite consideration of such complex expressions as



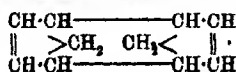
or the possibility of polymerisation being due to change in valence on the part of nitrogen, developing the structure



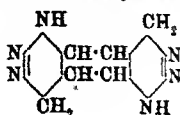
but it seems to us more probable that the case under consideration is allied to that of cyclopentadiene, which has been shown by Krieger and Spilker (*Ber.*, 1896, 29, 552) to undergo polymerisation with great facility, a change which they represent as follows:



aving in mind Thiele's theory of partial valency, and its applica-
to cyclopentadiene, the alternative:



rally suggests itself for the polymerised hydrocarbon, but the
ssity of maintaining the diazoamino-structure in the transformed
azoimide leads us to prefer the expression



that substance.

EXPERIMENTAL.

Allylazoimide, $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{N}_3$.

The interaction of sodium azide and allyl chloride or iodide was
flowed under various conditions in the hope of improving the
remunerative yields given by the earlier experiments, but we have
id to content ourselves with interrupting the process at a point when
e mixture of allylazoimide, its degradation products, and unchanged
yl haloid contains the maximum of triazo-hydrocarbon, which never
ceeded 30 per cent. Allyl chloride is more profitable than the
ide, not only on account of initial cost, but also because the boiling
nt is below that of allylazoimide.

Fifty grams of allyl chloride and 100 c.c. of alcohol were heated
der reflux on the water-bath with 50 grams of sodium azide in
0 c.c. of water during two hours, when nitrogen began to escape in
all quantities from the faintly yellow liquid, through which a rapid
rrent of steam was then passed; the distillate, diluted with much
ter, was extracted twice with ether, and the solvent, having been
ashed with dilute sulphuric acid to remove the basic products of
ansformation, was shaken several times with water and dried with
cium chloride. On fractionating with a long column of the rod-and-
sk pattern, the temperature rose gradually to 76° , and the fraction
sing over at $50\text{--}76^\circ$ gave, when twice distilled, a material which
iled steadily at $76\text{--}5^\circ$ under 760 mm. pressure. Using the foregoing
antities, the yield amounted to 15 grams, but was greatly reduced

further distillation, each repetition diminishing the quantity of
ylazoimide by about 15 per cent., owing to transformation into the
meride and its products of change. Although seemingly an
lividual and free from chlorine, the analysis, for which we are
debted to Mr. Richmond, gave results several per cent. too low, and

this must be attributed to loss of nitrogen in the form of hydrazic acid:

0.1544 gave 40.9 c.c. N_2 at 20.5° and 751 mm., along with 0.0 of ammonia. $N = 30.4$ as gas, 15.4 as NH_3 ; total, 45.8.

$C_3H_5N_3$ requires $N = 50.6$ per cent.

Allylazoisimide is a mobile, refractive liquid, having specific gravity 0.924 compared with water at 25° . The odour is allylaceous, but less powerful and much sweeter than that of allyl chloride, more closely resembling that of chloroform, whilst the vapour, when inhaled, produces the characteristic throbbing sensation at the base of the forehead. Concentrated sulphuric acid decomposes the azide with vigour, but potash does not liberate gas, although stannous chloride sets free nitrogen immediately; the vapour of allylazoisimide explodes when heated, but the detonation is mild.

oβ-Dibromo-γ-triazopropene, $CH_2Br \cdot CHBr \cdot CH_2 \cdot N_3$.

On adding a solution of bromine in chloroform to a mixture of allylazoisimide with the solvent, the calculated amount of halogen is decolorised without liberation of hydrogen bromide; after fifty minutes at zero, the liquid was washed with sodium carbonate and distilled in steam, which separated the chloroform from the dibromide. The latter was distilled twice under 5 mm. pressure, boiling steam at 87° :

0.3442 gave 29.55 c.c. N_2 at 18.7° and 754 mm., along with 0.01 of ammonia. $N = 9.95$ as gas, 5.63 as NH_3 ; total 15.57.

$C_3H_5N_3Br_2$ requires $N = 17.28$ per cent.

Mr. Richmond, to whom we owe the analysis, reported difficulty in measuring the gas, on account of the mercurous bromide produced, and it is probable that a certain proportion of the nitrogen is lost in this way.

The Diazoamino-compound, $(C_3H_5N_3)_2$, from Allylazoisimide.

Although a freshly-distilled specimen of allylazoisimide undergoes no change with dilute acids, the substance acquires in the course of a few hours the property of effervescing when mixed even with acetic acid. The change on which this alteration of character depends is accelerated by warming the substance to about 50° , and after one or more days, according to circumstances, the liquid deposits large, lustrous, transparent crystals. Recrystallisation from benzene was first attempted, one gram requiring about 400 c.c. of the boiling solvent, but loss of material occurred, and the crystals deposited on cooling, although colourless, were found to retain a basic odour; purification

effected by dissolving one gram in 30 c.c. of boiling chloroform to which 60 c.c. of petroleum (b. p. 60–80°) were then added. Snow-white, odourless plates were thus obtained, melting sharply and softening at 192°:

0.846 gave 0.2955 CO_2 and 0.1045 H_2O . $\text{C} = 43.65$; $\text{H} = 6.33$.

0.143 „ 49.3 c.c. N_2 at 16° and 767 mm. $\text{N} = 51.42$.

$\text{C}_5\text{H}_5\text{N}_3$ requires $\text{C} = 43.37$; $\text{H} = 6.01$; $\text{N} = 50.62$ per cent.

The analyses were somewhat complicated by the systematic presence of nitrous fumes, but Mr. Richmond has confirmed the nitrogen percentage by his method:

0.689 gave 20.1 c.c. N_2 at 15.7° and 746 mm., along with 0.01138 of ammonia. $\text{N} = 33.76$ as gas, 16.52 as NH_3 ; total, 50.28.

The diazoamino-compound dissolves more readily in acetone and in chloroform than in benzene, but it is sparingly soluble in ethyl alcohol and insoluble in petroleum. Estimation of molecular weight based on the boiling point of chloroform solutions gave 172 and 170, the formula $(\text{C}_5\text{H}_5\text{N}_3)_2$ requiring 166. Hot alcohol and boiling water decompose the substance slowly, although definite products could not be obtained; the decomposition by dilute acids proceeds in a manner analogous to that in which the aliphatic diazoamino-compounds described by Dimroth are degraded, two-thirds of the nitrogen being free:

0.1176 gave 34.6 c.c. N_2 at 19° and 748 mm. when treated with 5 per cent. hydrochloric acid. $\text{N} = 33.85$.

$\text{C}_5\text{H}_5\text{N}_3$ requires $2/3\text{N} = 33.75$ per cent.

Several attempts have been made to isolate from the bright red solution definite products of this change, but the small quantity of material at our disposal has prevented a conclusion from being reached. The liquid reduced cold Fehling's solution and ammoniacal silver oxide immediately, the original compound being indifferent to these reagents, but on evaporation the reducing properties disappeared, and the platinumchloride prepared from the residue was found to be that of ammonium. As might be expected from these indications of sensitive character, the product of decomposing the diazoamino-compound with acids did not form a stable salt with platinum tetrachloride, the yellow precipitate from which quickly became dark brown. The power to combine with phenylcarbimide, usually possessed by diazoamino-compounds of this class, is not displayed by the trans-allylazoimide, which was heated with the agent during twenty-four hours. Furthermore, alcoholic ammoniacal silver oxide did not form an insoluble derivative.

ROYAL COLLEGE OF SCIENCE, LONDON,
SOUTH KENSINGTON, S.W.

CXV.—*Aromatic Arsonic and Arsinic Acids*

By FRANK LEE PYMAN and WILLIAM COLEBROOK REYNOLD

FOR some time past we have been engaged in the preparation of derivatives of arsenic, and, as two recent publications (O. and R. A. *Ber.*, 1908, 41, 931; Benda and Kahn, *Ber.*, 1908, 41, 1672) show that there are other chemists covering somewhat the same ground, we have deemed it advisable to publish our results so far as they proceeded.

We had prepared 2-aminotolyl-5-arsonic acid and its acetyl derivative some months ago, and these substances together with sodium *p*-aminophenylarsonate have been tested physiologically and clinically. Ehrlich had shown that the toxicity of sodium *p*-acetylaminophenylarsonate is considerably less than that of sodium *p*-aminophenylarsonate, and the same relationship has now been found between the corresponding toluidine derivatives; sodium 2-aminotolyl-5-arsonate has about the same toxicity as sodium *p*-aminophenylarsonate, whilst that of sodium 2-acetylaminotolyl-5-arsonate is very considerably less. These substances have been specially intended for use in trypanosomiasis (sleeping sickness), and experiments on their effect on different strains of trypanosomes have shown that, whilst certain strains are destroyed by the treatment, others were more resistant. In the treatment of syphilis, however, these substances have proved especially efficacious, and the results obtained in this connexion are exceedingly promising. Since O. and R. Adler and Benda and Kahn (*loc. cit.*) have already published the method of preparation and physical properties of these substances, we need only state that we confirm their results, and supplement them by recording the statistics of the use of the sodium salts, this latter being important from the point of view of their use in medicine.

In the preparation of *p*-aminophenylarsonic acid and 2-aminotolyl-5-arsonic acid, we have obtained as by-products the corresponding bisaminoarylarsonic acids, which have been briefly alluded to by Benda and Kahn (*loc. cit.*), but, as these have been in our hands some time past, we give in this communication a full description of their preparation and properties. The constitution of these substances has been proved by replacing the arsenic acid residue by iodine according to the method used by Ehrlich and Berthelm (*Ber.* 1907, 40, 3292) for *p*-aminophenylarsonic acid.

The arsinic acids are now being investigated clinically with a view to their possible use in trypanosomiasis and syphilis, but the results are yet not sufficiently conclusive.

EXPERIMENTAL.

inotolyl-5-arsonic acid is stated by Benda and Kahn (*loc. cit.*) at 195°; we have found the melting point 198–200°. The action of this acid was readily shown by boiling it with dilute iodic acid and potassium iodide, when a good yield of 5-iodo-*o*-toluidine melting at 80–85° was obtained. After recrystallisation, the *o*-compound melted at 85° and its acetyl derivative at 168°, and both substances melted at the same temperatures when mixed with the substances prepared from aceto-*o*-toluidine.

Potassium *2-aminotolyl-5-arsenate* is obtained in glistening, tabular crystals containing three and a-half molecular proportions of water. Recrystallisation by mixing a highly concentrated aqueous solution three times its volume of alcohol. When crystallised from alcohol, however, it separates with five molecules of water of crystallisation:

540 air-dried salt (from alcohol) lost 0.0890 H₂O at 130°.
H₂O = 19.6.

C₇H₇O₄NaAsNa, 3½ H₂O requires H₂O = 19.9 per cent.

217 air-dried salt (from water) lost 0.1129 H₂O at 130°.
H₂O = 26.8

C₇H₇O₄NaAsNa, 5H₂O requires H₂O = 26.2 per cent.

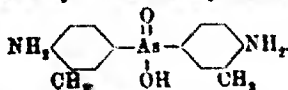
Potassium *2-acetylaminotolyl-5-arsenate* separates from alcohol 50 per cent. in glistening, tabular crystals, which contain five molecules of water of crystallisation. It crystallises from water, however, with seven molecules of water of crystallisation:

1774 air-dried salt (from alcohol) lost 0.1102 H₂O at 100°.
H₂O = 23.1.

C₉H₁₁O₄NaAsNa, 5H₂O requires H₂O = 23.4 per cent.

3210 air-dried salt (from water) lost 0.1560 H₂O at 100°.
H₂O = 29.9.

C₉H₁₁O₄NaAsNa, 7H₂O requires H₂O = 29.9 per cent.

Preparation of Bis-2-aminotolyl-5-arsinic Acid,

Two hundred grams of air-dried *o*-toluidine arsenate and 400 grams of *o*-toluidine were heated over a free flame with constant shaking until the mixture became fluid, and then gently boiled under a reflux condenser for one hour, the heat being regulated so that a thermo-

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In the preparation of *p*-aminophenylarsonic acid and 2-aminotolyl-5-arsonic acid, we have obtained as by-products the corresponding bisaminoarylsinic acids, which have been briefly alluded to by Benda and Kahn (*loc. cit.*), but, as these have been in our hands some time past, we give in this communication a full description of their preparation and properties. The constitution of these substances has been proved by replacing the arsenic acid residue by iodine according to the method used by Ehrlich and Berthelm (*Ber.* 1907, 40, 3292) for *p*-aminophenylarsonic acid.

The arsinic acids are now being investigated clinically with a view to their possible use in trypanosomiasis and syphilis, but the results as yet not sufficiently conclusive.

EXPERIMENTAL.

5-aminotolyl-5-arsonic acid is stated by Benda and Kahn (*loc. cit.*) at 195°; we have found the melting point 198–200°. The action of this acid was readily shown by boiling it with dilute hydrochloric acid and potassium iodide, when a good yield of 5-iodo-*o*-toluidine melting at 80–85° was obtained. After recrystallisation, the compound melted at 85° and its acetyl derivative at 168°, and both substances melted at the same temperatures when mixed with the substances prepared from aceto-*o*-toluidide.

Am 2-aminotolyl-5-arsenate is obtained in glistening, tabular crystals containing three and a-half molecular proportions of water. Crystallisation by mixing a highly concentrated aqueous solution with three times its volume of alcohol. When crystallised from water, however, it separates with five molecules of water of crystallisation:

740 air-dried salt (from alcohol) lost 0.0890 H₂O at 130°. H₂O = 19.6.

C₇H₉O₄NaAsNa, 3½ H₂O requires H₂O = 19.9 per cent.

717 air-dried salt (from water) lost 0.1129 H₂O at 130°. H₂O = 26.8

C₇H₉O₄NaAsNa, 5H₂O requires H₂O = 26.3 per cent.

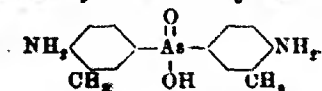
Am 2-acetylamino-5-arsenate separates from 50 per cent. aqueous alcohol in glistening, tabular crystals, which contain five molecules of water of crystallisation. It crystallises from water, however, with seven molecules of water of crystallisation:

774 air-dried salt (from alcohol) lost 0.1103 H₂O at 100°. H₂O = 23.1.

C₉H₁₁O₄NaAsNa, 5H₂O requires H₂O = 23.4 per cent.

7210 air-dried salt (from water) lost 0.1560 H₂O at 100°. H₂O = 29.9.

C₉H₁₁O₄NaAsNa, 7H₂O requires H₂O = 29.9 per cent.

Preparation of Bis-2-aminotolyl-5-arsinic Acid,

To one hundred grams of air-dried *o*-toluidine arsenate and 400 grams of *o*-toluidine were heated over a free flame with constant shaking until the mixture became fluid, and then gently boiled under a reflux condenser for one hour, the heat being regulated so that a thermo-

meter immersed in the liquid registered 180—185°. The mixture was allowed to cool, and extracted with a 10 per cent. solution of sodium carbonate as long as effervescence occurred. The solution was then evaporated until crystallisation commenced, and allowed to cool. The first crop of sodium 2-aminotolyl-5-arsinate was then separated, well washed with alcohol, and set aside. The mother liquor and alcoholic washings were combined and evaporated to a thick syrup, and this was mixed with several times its volume of alcohol. A second crop of sodium 2-aminotolyl-5-arsinate was precipitated, and this was also separated, washed with alcohol, and set aside. The final mother liquors, together with the alcoholic washings, on evaporation to remove the alcohol and subsequent precipitation by hydrochloric acid gave 15 grams of a purple substance, which was dissolved in aqueous sodium hydroxide, evaporated to a small bulk, and allowed to cool, when a quantity of large, prismatic needles separated from the deep-red liquor. These were purified by several crystallisations from water, and proved to be sodium 2-aminotolyl-5-arsinate. The quantity of salt actually isolated in pure state amounted to 6 grams, which represents 3 per cent. of the theoretical, but a considerable quantity, possibly as much as 10 per cent., remained in the deep-red, syrupy mother liquors.

Bis-2-aminotolyl-5-arsinic acid is obtained by adding the calculated quantity of a mineral acid to the solution of its sodium salt. On crystallisation from boiling water, it forms highly refracting, prismatic microscopic needles, which melt and decompose at 247—249°. It is practically insoluble in cold water and the usual organic solvents, but is fairly easily soluble in glacial acetic acid. It is readily soluble in dilute alkalis or mineral acids:

0.1724 gave 0.3332 CO_2 and 0.0840 H_2O . $\text{C} = 52.7$; $\text{H} = 5.5$.

0.0726 " 5.5 c.c. N_2 at 21° and 763 mm. $\text{N} = 8.7$.

$\text{C}_{14}\text{H}_{17}\text{O}_2\text{N}_2\text{As}$ requires $\text{C} = 52.5$; $\text{H} = 5.4$; $\text{N} = 8.7$ per cent.

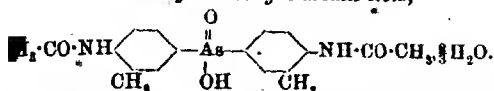
The acid gave a good yield of 5-iodo-*o*-toluidine (m. p. 80—81°) when boiled with dilute sulphuric acid and potassium iodide. A recrystallisation, this iodo-compound melted at 85° and its acid derivative at 168°, and both substances melted at the same temperatures when mixed with the pure substances prepared from acetone and *o*-toluidide.

The sodium salt, which separates from its aqueous solution in large, hard, prismatic needles, melts in its water of crystallisation at 74—75°, and on further heating loses water, re-solidifies, and does not then melt at 250°. It dissolves in one and a-half times its weight of water at 16°, giving an alkaline solution, and is very easily soluble in alcohol. It contains seven and a-half molecular proportions

of crystallisation, of which five are lost at 100° and the rest at 130°:

- 6 air-dried salt lost 0.0718 H₂O at 100°. H₂O = 18.5.
 8 " " " 0.1028 H₂O " 130°. H₂O = 28.3.
 1/2 N₂AsNa, 7 1/2 H₂O losing 5 H₂O requires H₂O = 18.9 per cent.
 1/2 N₂AsNa, 7 1/2 H₂O " 7 1/2 H₂O " H₂O = 28.3

Bis-2-acetylaminotolyl-5-arsinic Acid,



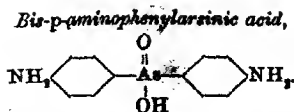
ty grams of bis-2-aminotolyl-5-arsinic acid were mixed with
 ms of acetic anhydride and allowed to stand. After a few
 a violent reaction took place, resulting in a clear solution.
 id was poured into 250 c.c. of water, and, on scratching,
 ns of white crystals separated. A second crop of 6 grams
 tained by evaporation of the mother liquor; the total yield,
 ns, represents 71 per cent. of the theoretical.

Bis-2-acetylaminotolyl-5-arsinic acid crystallises from boiling water
 ily refracting, microscopic prisms and melts at 242—244°. It
 ically insoluble in cold water and the usual organic solvents,
 ily easily soluble in glacial acetic acid. It is readily soluble
 alkalis, but is insoluble in dilute acids. The acid separates
 ueous solutions with two-thirds of a molecular proportion of
 of crystallisation:

- 6 air-dried salt gave 0.3148 CO₂ and 0.0772 H₂O. C = 51.8;
 H = 5.2.
 10 air-dried salt lost 0.0124 H₂O at 150°. H₂O = 3.0.
 8 dried at 150° gave 0.3698 CO₂ and 0.0908 H₂O. C = 53.1;
 H = 5.4.
 O₄N₂As, 3/2 H₂O requires C = 51.9; H = 5.4; H₂O = 2.9 per cent.
 C₁₈H₂₁O₄N₂As requires C = 53.4; H = 5.2 per cent.

sodium salt crystallises from water in radial clusters of silky
 ; it melts in its water of crystallisation at 106—107, and on
 heating resolidifies and does not then melt at 250°. It dis-
 in twice its weight of water at 16°, giving an alkaline solution,
 very easily soluble in alcohol. It contains six molecules of
 of crystallisation:

- 3 air-dried salt lost 0.0393 H₂O at 150°. H₂O = 20.2.
 C₁₈H₂₀O₄N₂AsNa, 6 H₂O requires H₂O = 20.2 per cent.



This acid results as a by-product in the preparation of phenylarsonic acid by Bechamp's method (*Compt. rend.*, 1173). It is most readily isolated in the following manner: product obtained by heating aniline arsenate with excess of at 180° is extracted with 10 per cent. sodium carbonate, the aqueous solution concentrated, and completely precipitated with hydrochloric acid. The precipitate is then digested with just enough aqueous sodium hydroxide to give a faintly alkaline solution, filtered from the undissolved matter, which consists of the free arsinic acid. The latter is then converted into the barium salt, which is crystallised several times from water, using animal charcoal until colourless. The pure barium salt is dissolved in water, mixed with the calculated quantity of hydrochloric acid, and the free arsinic acid is obtained as a dense, white precipitate of melted. The yield amounts to about 2—3 per cent. of the theoretical.

Bis-p-aminophenylarsinic acid melts and decomposes at 248° . It is very sparingly soluble in water and the usual organic solvents, moderately so in glacial acetic acid, and readily so in dilute acids:

0.1358 gave 0.2440 CO_2 and 0.0534 H_2O . $\text{C} = 49.0$; $\text{H} = 4.5$.
 $\text{C}_{12}\text{H}_{12}\text{O}_2\text{N}_2\text{As}$ requires $\text{C} = 49.3$; $\text{H} = 4.5$ per cent.

The acid gave a good yield of *p*-iodoaniline (m. p. $62-63^{\circ}$) boiled with sulphuric acid and potassium iodide.

The sodium salt crystallises from water in large, monoclinic prisms and melts in its water of crystallisation at 83° , after sintering at 75° onwards. On further heating, it loses water, resolidifies, and then melts at 250° ; it is soluble in an equal weight of water, giving an alkaline solution, and is very soluble in alcohol. It contains a slightly variable amount of water of crystallisation, the amount obtained on analysis lying between those required for five and six molecular proportions:

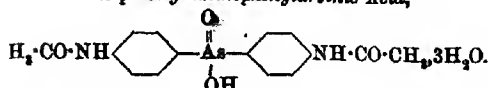
0.3979 air-dried salt lost 0.0928 H_2O at 120° . $\text{H}_2\text{O} = 23.3$.
 0.2450 " " " 0.0591 H_2O " 120° . $\text{H}_2\text{O} = 24.1$.
 0.2492 " " " 0.0616 H_2O " 120° . $\text{H}_2\text{O} = 24.7$.
 $\text{C}_{12}\text{H}_{12}\text{O}_2\text{N}_2\text{AsNa}_2 \cdot 5\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 22.3$ per cent.
 $\text{C}_{12}\text{H}_{12}\text{O}_2\text{N}_2\text{AsNa}_2 \cdot 6\text{H}_2\text{O}$ " $\text{H}_2\text{O} = 25.6$

rium salt, which crystallises from water in large, hard crystals containing seven and a-half-molecular proportions of water of crystallisation; it is soluble in twice its weight of cold water, giving a solution, and is sparingly soluble in alcohol:

air-dried salt lost 0.0404 H_2O at 180° . $\text{H}_2\text{O} = 15.8$.

$(\text{H}_{12}\text{O}_4\text{N}_2\text{As})_2\text{Ba}, 7\frac{1}{2}\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 15.8$ per cent.

Bis-p-acetylaminophenylarsinic Acid,



acid is obtained in an almost quantitative yield by the action of acetic anhydride on bis-p-aminophenylarsinic acid. It crystallises from water in rosettes of needles, and melts at 275° . It is very slightly soluble in the usual organic solvents or cold water, so in boiling water, and moderately so in glacial acetic acid. It separates from aqueous solution with three molecules of water on crystallisation:

2 air-dried salt lost 0.0312 H_2O at 120° . $\text{H}_2\text{O} = 12.3$.

0 dried at 120° gave 0.3484 CO_2 and 0.0740 H_2O . $\text{C} = 51.1$;

$\text{H} = 4.5$.

$\text{C}_{18}\text{H}_{17}\text{O}_4\text{N}_2\text{As}, 3\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 12.6$ per cent.

$\text{C}_{18}\text{H}_{17}\text{O}_4\text{N}_2\text{As}$ requires $\text{C} = 51.1$; $\text{H} = 4.6$.

sodium salt, which separates from water in prismatic needles, loses about 50° in its water of crystallisation, and on further heating loses water, resolidifies, and does not then melt at 250° . It is soluble in an equal weight of cold water, giving an alkaline solution, and is readily soluble in alcohol. It contains nine molecules of water of crystallisation:

2 air-dried salt lost 0.0908 H_2O at 140° . $\text{H}_2\text{O} = 29.2$.

$\text{C}_{16}\text{H}_{16}\text{O}_4\text{N}_2\text{AsNa}, 9\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 28.9$ per cent.

WELLCOME CHEMICAL WORKS,
DARTFORTH, KENT.

CXVI.—*The Electrolytic Oxidation of Some Hydroxybenzoic Acids.*

By ARTHUR GEORGE PERKIN and FREDERICK MOLLWO PERKIN.

It has been previously shown that when gallic acid (Trans. 83, 199) is oxidised by means of potassium ferricyanide in presence of sodium acetate, a compound is formed which, judging from its properties, is probably purpurogallincarboxylic acid. Unfortunately, the amount of product so obtained was far too small to admit of any extended investigation, but, as it was subsequently ascertained that purpurogallin itself can be very conveniently prepared by the electrolytic oxidation of pyrogallol under certain circumstances (Trans., 1904, 85, 243), a study of the behaviour of gallic acid in this respect was also instituted. As a result, considerably larger yields of purpurogallincarboxylic acid were obtained, and by a further investigation of the process a still greater improvement in this respect has been effected. The main results of this work have been completed for some time, but their communication has been delayed in the hope that the constitution of purpurogallin itself would have been elucidated. An important point in this respect has been the fact that the product of the oxidation is probably the compound $C_6H_4O_5$ (Trans., 1906, 89, 803), which appears to be a hydroxy-*o*-benzoquinone. It is obtained by the action of amyl nitrite on an alcoholic solution of pyrogallol, for this in boiling aqueous solution is partly converted into purpurogallin. A preliminary account of the further study of this colouring matter itself has been given (Proc., 1905, 21, 212), but the continuation of the investigation was postponed until other work of more pressing character had been completed. The investigation is now being undertaken afresh, but, as some time may elapse before the results of special interest accumulate, it seemed advisable to communicate to the Society the points enumerated in the following pages.

Electrolytic Oxidation of Gallic Acid.

1. *Electrolyte:—Sodium Sulphate.*

The first experiments were made under practically similar conditions to those which had given the most satisfactory results in the electrolytic oxidation of pyrogallol. The gallic acid was dissolved in a 15 per cent. solution of sodium sulphate slightly acidified with sulphuric acid, but, owing to its sparing solubility, only comparatively dilute solutions could be used. Twenty grams of

dissolved in 1 litre of 15 per cent. sodium sulphate solution, 5 c.c. of 4*N*-sulphuric acid were added. In order to obtain it was found necessary to grind up the gallic acid into a thin slurry in water, and to add this to the sodium sulphate solution. The mixture was then agitated by means of a glass stirrer until the gallic acid had completely dissolved, the sulphuric acid was then added, and the solution electrolysed. As anodes two pieces of sheet platinum of an area of 750 sq. cm. were used, the total anode surface being therefore 1.5 sq. dm. The cathode consisted of a lead paddle of surface of 0.5 sq. dm., which during the electrolysis was driven by means of a small electromotor. It should be mentioned

that preliminary experiments had shown that the best results were obtained when the anode and cathode compartment were not separated. In order to prevent rise of temperature, the electrolysis was carried out in a vessel placed in an outer vessel through which cold water was circulated. A current of 4 amperes was passed for seven hours, the E.M.F. being 5 volts. When the action commenced, the solution became gradually darkened, and at the end of fifteen minutes a black liquid had been produced.

When the electrolysis was finished, the mixture was allowed to stand for 24 hours, when a fine black precipitate had settled to the bottom of the vessel. The precipitate was collected, repeatedly washed with cold water until the wash-water was colourless, and drained on a porous tile. The percentage yield of the product was 34 per cent. of the gallic acid employed. This method of procedure gives the free acid. It was afterwards found, however, that better results were obtained when sodium acetate was employed, the sparingly soluble sodium salt of the acid being thus formed. Experiments were also tried with potassium, calcium, strontium, and magnesium acetates, but the yields were in no case so high as when sodium acetate was employed, and the product was not

2. *Electrolyte:—Sodium Acetate.*

Twenty grams of gallic acid were ground into a paste with a 15 per cent. solution of sodium acetate. The paste was then poured into a beaker of the same solution, well stirred, and the clear liquid decanted. The residue was washed with the same electrolyte. The solution became yellow on the passage of the current, but gradually darkened, and finally assumed a brownish-black tint. The current employed was 2.5–3 amperes with an E.M.F. of 5–6 volts, and the electrolysis was continued for about eight hours. After standing for 24 hours, the precipitate was collected, washed with cold water, and dried with alcohol. The yield varied between 30 and 40 per cent. of the acid taken.

The product of oxidation consisted of an orange-brown, or powder, which, under the microscope, was seen to consist of thin leaflets, and was evidently a sodium salt. An analysis of substance, dried at 160° , indicated that it is an almost pure *purpurogallincarboxylate*.

Found: Na = 7.85.

$C_{12}H_7O_7Na$ requires Na = 8.04 per cent.

A determination of the water of crystallisation found to be in this preparation was made at 160° on a sample which had dried in the air for several days. The analysis showed it to $4H_2O$:

Found: $H_2O = 20.0\%$.

$C_{12}H_7O_7Na \cdot 4H_2O$ requires $H_2O = 20.11$ per cent.

In the anhydrous condition, this substance is hygroscopic, standing overnight, regained one molecule of water:

Found: $H_2O = 5.00$.

Theory requires $H_2O = 5.92$ per cent.

Sodium purpurogallincarboxylate is sparingly soluble in boiling and from a concentrated solution is deposited on cooling in microneedles, which contain no water of crystallisation. When with a boiling aqueous solution of potassium acetate, the filtrate on cooling, deposits the potassium salt in prismatic needles resembling *purpurogallin* itself. An analysis of this compound at 160° , gave:

Found: K = 12.95.

$C_{12}H_7O_7K$ requires K = 12.91 per cent.

The air-dried substance, heated to 160° , loses three molecules of crystallisation:

Found: $H_2O = 15.16, 15.37$.

$C_{12}H_7O_7K \cdot 3H_2O$ requires $H_2O = 15.17$ per cent.

A boiling aqueous solution of potassium *purpurogallincarboxylate* on cautious treatment with barium chloride, deposits orange-red, prismatic needles, which consist of the corresponding barium salt, almost insoluble in water. When dried at 160° , it

Found: Ba = 20.96.

$(C_{12}H_7O_7)_2Ba$ requires Ba = 20.66 per cent.

When these salts are decomposed with boiling dilute hydrochloric acid, *purpurogallincarboxylic acid* is obtained as a semi-gel precipitate, which, after drying, is but sparingly soluble in any usual solvents. From nitrobenzene, it is deposited as small, coloured needles, but, as a very large amount of the solvent was necessary for the preparation of even a gram in this condition,

method of purification was desirable. The difficulty was over-employing the crude acid recently precipitated from its sodium moist condition, as this dissolved somewhat readily in boiling. On partly evaporating the solution, crystals separated on which were collected while the mixture was still warm and with dilute alcohol. A chemically pure product could thus be obtained in one such operation, but, if further purification was the product was again rendered soluble in alcohol by reprecipitation and crystallised in a similar manner:

$C = 54.37$; $H = 3.24$.

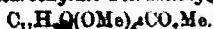
$C_{11}H_8O_7$ requires $C = 54.54$; $H = 3.03$ per cent.

Progallincarboxylic acid usually crystallises in minute, orange-leaflets, which are devoid of water of crystallisation, does not melt below 300° , and on strong heating yields a trace of a crystalline residue, apparently consisting of the unchanged acid. Occasionally it is deposited from dilute alcohol in needles, and it is possible that this variety, although but rarely obtained, water of crystallisation is present. As previously stated, this compound (Trans., 1903, 1904) gives with alkaline solutions the characteristic colour reactions of *progallin* itself, and, moreover, possesses strong mordant dyeing properties, which closely resemble those given by the same colouring matter.

Further attempts to prepare the acetyl derivative in a pure form have been unsuccessful; the product hitherto obtained being, though enough, too soluble to admit of crystallisation.

It is readily attacked by bromine in the presence of acetic acid or other acids, but no sparingly soluble derivative of the nature of dibromoprogallin is thus formed. Up to the present a definite product of bromination has not been isolated, but, as apparently in this manner both bromination and decomposition simultaneously occur, the reaction will be more readily effected with a larger quantity of material, when this is available.

Purpurogallincarboxylate Tetramethyl Ether,



Purpurogallincarboxylic acid, or the crude sodium salt, electrochemically prepared and suspended in methyl alcohol, was treated with small quantities of methyl sulphate and concentrated potassium hydroxide solution until a final addition of the latter did not produce any more coloration. The methylation did not proceed readily, a large excess of the reagents being necessary for its completion, resembling one of the behaviours of alizarin in similar circumstances.

The product was poured into ether, the ethereal liquid well washed with dilute alkali, evaporated, and the residue purified by reprecipitation from alcohol. The yield was approximately 25 per

Found: C = 61.08; H = 5.70; OH, = 21.91.

$C_{17}H_{18}O_7$ requires C = 61.07; H = 5.39; OH, = 22.45 per

It consists of very pale yellow, almost colourless needles at 120–121°, sparingly soluble in alcohol, and resembling gallin tetramethyl ether.

To determine if this compound was an ester, it was digested with boiling dilute alcoholic potash for a few minutes. Addition did not cause the separation of a precipitate, and the clear liquid was neutralised with acid. On cooling, fine needles separated, were collected and recrystallised from dilute alcohol:

Found: C = 59.93; H = 5.12; OH, = 18.40.

$C_{16}H_{16}O_7$ requires C = 60.00; H = 5.00; OH, = 18.75 per

Purpurogallincarboxylic acid tetramethyl ether, $C_{11}H_8O(OMe)_4$ consists of small, faintly-yellow needles, melting at 15°, readily soluble in alcohol, and more sparingly so in benzene, in which it crystallises in minute needles.

Purpurogallonecarboxylic Acid, $C_{11}H_8O_5 \cdot CO_2H$.

It was previously shown by Perkin and Steven (*loc. cit.*) that purpurogallin is digested with boiling 50 per cent. aqueous potassium hydroxide, it is converted into two isomeric compounds having the same formula as purpurogallin itself, and it was therefore intended to determine if a similar change occurs when purpurogallonecarboxylic acid is so treated. A solution of 3 grams of the acid in 10 c.c. of the potassium hydroxide solution was boiled in an open flask. A test portion on dilution with water did not develop a green coloration. The product, when cautiously treated with dilute sulphuric acid, deposited an orange-colored, sandy precipitate, which on filtration under the microscope was seen to consist of fine needles. These were collected, dissolved in boiling alcohol, the solution poured into ether, and, after removal of insoluble matter, the ethereal liquid well washed with water and evaporated. The concentrated solution of the residue at first deposited a trace of uncrystallisable purpurogallincarboxylic acid, which was removed, and the addition of a little boiling water to the filtrate now caused the separation of bright yellow needles. These were further purified by crystallisation from dilute alcohol:

Found: C = 54.81; H = 3.27.

$C_{12}H_8O_7$ requires C = 54.54; H = 3.03 per cent.

As thus prepared, the substance appeared to be homogeneous, and no two distinct forms could be separated, as was previously found to be the case with the product obtained from purpurogallin itself.

ly precipitated moist condition, *purpureogallonecarboxylic acid* is readily soluble in boiling alcohol, and on evaporating the acid separates in the crystalline condition. When fractionally crystallized in this manner, the first deposit contained but a trace (2.48 per cent.) of water of crystallisation, whereas in the second, approximately 10 molecules of water of crystallisation were present :

$H_2O = 11.27, 11.15, 11.88.$

$C_{12}H_8O_7 \cdot 2H_2O$ requires $H_2O = 12.0$ per cent.

The anhydrous variety is sparingly soluble in hot alcohol, but the hydrated form readily passes into solution, but, if the latter when dissolved is digested at the boiling point, the solution quickly becomes semi-solid, owing to the separation of the anhydrous acid. Under the microscope both varieties were seen to consist of needle-like crystals, and no special difference could be observed between them. *Purpureogallonecarboxylic acid* does not melt below $100^\circ C$, and is soluble in alkalis with a yellow colour, which, on exposure to air, becomes deep crimson-red. If air is passed through the liquid until the latter tint is fully developed, the solution is extracted with ether, and the extract evaporated, an orange-red residue is obtained, which on drying intumesces in the manner characteristic of the tannins. *Purpureogallinecarboxylic acid*, in a similar manner, gives an analogous product, but attempts to obtain these compounds in a pure condition have been hitherto unsuccessful. *Purpureogallonecarboxylic acid* dyes mordanted wool cloth almost identical with those given by the *purpureogallones*.

Aluminium.	Tin.	Iron.
Dark brown	Pale yellow	Chocolate-brown

alcoholic lead acetate, it gives a yellow precipitate, and with ferric chloride a deep brownish-black coloration.

of Acetic Anhydride.—The acid (1 gram) is but slowly attacked by boiling acetic anhydride (10 c.c.), but on addition of a few drops of pyridine a clear liquid is almost instantaneously formed, and the reaction is complete after a few minutes' time. On pouring into water, an oily product separated, which

as noted in previous work with ellagic and flavellagic acids (*loc. cit.*) that, these compounds are but slowly attacked by acetic anhydride when in the solid state, if pyridine of crystallisation was present the production of the acetyl derivatives was much more rapid. Experiments carried out with numerous substances indicated that pyridine employed in the above manner greatly facilitates the acetylation process, and in every case was preferable to the employment of acetic anhydride. With compounds of the nature of alizarin or quercetin, which are sparingly soluble acetyl derivatives, and employing the usual quantity of reagents, only six or ten drops of pyridine for one gram of the phenol are

rapidly became crystalline, and this was collected and, in the earlier experiments, purified by crystallisation from alcohol, in which it is sparingly soluble. Curiously enough, however, much loss occurs during the latter treatment, a yield of only 15 per cent. being thus obtained, but this loss was subsequently avoided by crystallisation from a mixture of benzene and nitrobenzene:

Found: C = 58.10; H = 3.24.

$C_{12}H_4O_6(C_2H_5O)_2$ requires C = 58.18; H = 3.03 per cent.

During the acetylation therefore of purpurogallonecarboxylic acid, a molecule of water is simultaneously removed, which was also (*loc. cit.*) shown to be the case when purpurogallones themselves were similarly treated. An estimation of the acetyl groups was carried out by the ethyl acetate method (Trans., 1905, 87, 107):

Found: $C_2H_4O_2$ = 37.81.

Theory requires $C_2H_4O_2$ = 38.21 per cent.

During the hydrolysis, the acetyl compound unites with a molecule of water and is reconverted into purpurogallonecarboxylic acid, which is readily isolated by cautious addition of boiling water to the residual alcoholic liquid. *Acetylanhydropurpurogallonecarboxylic acid* forms colourless needles, melting at 236–238° with effervescence.

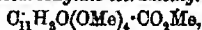
It has previously been shown (*loc. cit.*) that when isopurpurogallone is dissolved in sulphuric acid, the anhydro-compound, $C_{11}H_6O_4$, is formed, and can be isolated by means of acetic acid. Experiments with the acid in a similar manner gave, however, a yellow product, which consisted of the unaltered compound, as analysis showed:

Found: C = 54.56; H = 3.52 per cent.

Although judging by the results of the acetylation there is every reason to suppose that the acid $C_{11}H_6O_4 \cdot CO_2H$ is formed by the action of the sulphuric acid, it is evidently of a less stable nature than the corresponding isopurpurogallone derivative, $C_{11}H_6O_4$, and readily regenerates the purpurogallonecarboxylic acid during the process employed for its isolation. Such a change evidently takes place, although less readily, when the acetyl derivative is dissolved in alcohol, but this can be avoided, as shown above, by the employment of a solvent in which the absence of water can be ensured.

necessary. The pyridine is added to the boiling mixture, and the reaction is completed by digestion for a few minutes. On treating the product with alcohol, the acetyl compound separates in a crystalline condition, and is frequently thus isolated in a state of chemical purity. In cases where the acetyl compound is of a more soluble nature, precipitation with water and procedure in the usual manner is adopted.

Methyl purpurogallonecarboxylate tetramethyl ether,



can be obtained in an identical manner to that employed for the preparation of the corresponding ether of methyl purpurogallinocarboxylate. In this case, also, very large quantities of methyl sulphate and alkali are necessary, and the yield is poor. After removal of products soluble in alkali, the residue consisted principally of the anticipated compound, but a trace of a second methyl ether, too small in quantity for characterisation, was also present. By extraction with light petroleum, the latter remained undissolved, and, on concentrating the extract and cooling, colourless prisms separated, which melted at 110—111°:

Found: C = 61.27; H = 5.55; CH_2 = 21.69.

$C_{17}H_{18}O_7$ requires C = 61.08; H = 5.39; CH_2 = 22.45 per cent.

It was noted that the hydriodic acid liquid from the Zeisel determination contained crystals of purpurogallonecarboxylic acid.

Purpurogallonecarboxylic acid tetramethyl ether, $C_{11}H_8O(OMe)_4 \cdot CO_2H$, is produced, as might be anticipated, by a short digestion of the ester compound with alcoholic potash. On addition of water, the liquid remained clear, and when this was neutralised with acid an oil separated which rapidly became solid. It was purified by crystallisation from benzene, from which it is deposited as small, colourless needles:

Found: C = 60.13; H = 5.15.

$C_{16}H_{16}O_7$ requires C = 60.00; H = 5.00 per cent.

From alcohol, in which it is readily soluble, it crystallises in colourless prisms. It melts at 166—167°, and on treatment with hydriodic acid is converted into purpurogallonecarboxylic acid. By prolonged digestion with boiling alcoholic potash, this tetramethyl ether is not further attacked, and it thus appears evident that only one carboxyl group is present in this compound. The suggestion which was made in the earlier paper (*loc. cit.*) that the formation of the purpurogallones from purpurogallin was probably due in part to the oxidation of an alcoholic to a carboxylic group, cannot thus be considered feasible.

A study of the oxidation products of purpurogallin tetramethyl ether and of the corresponding derivative of purpurogallinocarboxylic acid will be shortly undertaken, as it is hoped that the constitution of these interesting compounds will thus be elucidated.

*The Electrolytic Oxidation of Gallic and Protocatechuic Acids
in the Presence of Sulphuric Acid.*

It has been previously shown (Trans., 1905, 87, 1412; 1906, 89, 251) that when gallic acid is oxidised with potassium persulphate in the presence of sulphuric acid, it is converted into ellagic acid and flavellagic acid (hydroxyellagic acid). On the other hand, when 60 per cent. sulphuric acid is employed, flavellagic acid is alone produced, and, again, if a mixture of acetic and sulphuric acids forms the solvent, ellagic acid alone is obtained. With the simpler hydroxybenzoic acids, similarly constituted compounds, but containing fewer hydroxyl groups, are produced, whereas the highest member of the series, dihydroxyellagic acid, is formed by heating ellagic acid with sulphuric acid to a high temperature. It appeared interesting to study the electrolytic oxidation of these acids in case any new points of interest might be revealed, although it seemed probable from a somewhat early patent dealing with this subject, which, however, we did not see until the work was nearly completed (Badische Anilin- und Soda-Fabrik, D.R.P. 85390), that the reaction was likely to follow the same lines as when persulphate was employed.

Gallic Acid.

The solution employed in these experiments was prepared by first stirring finely-powdered gallic acid (20 grams) with sulphuric acid until a thin cream was produced, and subsequently diluting with the acid until the volume of the mixture was about 90 c.c. From 10 to 15 c.c. of water were added, and the whole was then warmed until a clear liquid was obtained. Preliminary experiments carried out without a separation of the anode and cathode compartments gave an indifferent yield of the oxidation product, and the effect was now studied of separating the anode and cathode by means of a porous cell. A small beaker was therefore employed for the anode solution, and the cathode solution was contained in a porous cell, which was placed in the centre of the beaker, rise of temperature being avoided by standing the arrangement in a basin through which cold water was circulated. As the results, however, were still disappointing, the sheet anode was removed, and one consisting of coiled platinum wire having a total active surface of 5 sq. cm. was substituted, and by this means a very much better yield of the oxidation product was obtained. In the first experiments, the anode current density was 4 amperes per sq. decm., the E.M.F. being 4.5—5.3 volts, whereas in the latter it was 40 amperes per sq. decm. and the E.M.F. 6—7 volts. Care was taken not to allow the temperature to rise above 20°. As the best results were obtained with

a high current density, and, as with the concentration of the sulphuric acid used this would represent favourable conditions for the formation of persulphuric acid, it is probable that the oxidation is not directly electrolytic, but is due to the action of the persulphuric acid first produced.

According to the equation



20 grams of gallic acid would require the passage of six ampere-hours, but it was found more advantageous to pass the current for eight ampere-hours. The product was heated to 50° for one hour, poured into a large excess of water, and the precipitate collected and well washed. The average yield was 20 per cent., but occasionally as much as 30 per cent. of the substance was obtained.

Subsequently, a third method was employed, which gave a still better result. In this case the anode consisted of a platinum U-tube with a diameter of 0.33 cm. and having a total active surface of 9 sq. cm., and this was placed in the porous cell which now constituted the anode compartment. During the electrolysis, water was passed through the tube, so that, not only the solution, but the electrode itself was thus kept cold. The cathode consisted of a platinum wire which surrounded the anode cell, and with a current of 2 amperes the E.M.F. varied between 7 and 8 volts, the current density being therefore 0.22 ampere per sq. cm. By this method, it was possible to obtain a yield of 40 per cent. of the oxidation product, although owing to the small size of the platinum tube employed it was not possible to work with large quantities of material.

The product of the reaction consisted of a greenish-yellow powder of an apparently pure character, very sparingly soluble in the usual solvents, and readily soluble in alkalis with a well-marked green tint. It was evidently not identical with the compound described in the patent of the Badische Anilin- und Soda-Fabrik (*loc. cit.*), as prepared by the oxidation of gallic acid in the presence of sulphuric acid, for the latter has the property of giving a blue coloration with sodium carbonate solution.

For purification, crystallisation from pyridine was resorted to, a very large quantity of the solvent being necessary. The solution, on cooling, deposited a voluminous mass of small, yellow needles containing pyridine of crystallisation. These were collected, washed with pyridine, and finally with alcohol, by which latter treatment the crystals shrunk to a very small bulk. The product was dried at 160°:

Found: C = 52.80; H = 2.12.

$C_{14}H_6O_9$ requires C = 52.83; H = 1.89 per cent.

It did not melt below 360°, gave with nitric acid the Griessmayer

reaction, and evidently consisted of flavellagic acid. To prepare the acetyl derivative, the finely-powdered substance suspended in much boiling acetic anhydride was treated with a few drops of sulphuric acid, and the mixture digested at the boiling point for fifteen minutes. The clear liquid, on boiling, became semi-solid, owing to the separation of long, hair-like, colourless needles, which were collected and recrystallised from acetic anhydride:

Found: C = 54.59; H = 3.51.

$C_{14}H_4O_6(C_2H_5O)_2$ requires C = 54.54; N = 3.03 per cent.

It melted at $317-319^\circ$, and consisted without doubt of acetyl-flavellagic acid.

It is consequently evident that when a solution of gallic acid in 60 per cent. sulphuric acid is oxidised either electrolytically or by means of persulphates, the same compound, namely, flavellagic acid, is produced.

Protocatechuic Acid.

The method of procedure in this case was similar to that employed for the oxidation of gallic acid. The protocatechuic acid was dissolved in concentrated sulphuric acid, and the solution then diluted by the addition of a small quantity of water. The anode was a spiral of platinum wire having a surface of 5 sq. cm., and a current density of 20 amperes per sq. dm. was employed. When the electrolysis was complete, the product was heated to 50° for an hour, poured into water, and the precipitate collected and washed; the yield, however, was poor, and in no case was more than 10 per cent. of the oxidation product obtained.

The substance, which consisted of a pale brown, crystalline powder, was evidently of a much purer character than that usually obtained by means of persulphates. On account of its sparing solubility, it was acetylated with a large volume of acetic anhydride to which a small quantity of sulphuric acid had been added. The product was purified by recrystallisation from acetic anhydride;

Found: C = 60.82; H = 3.48.

$C_{14}H_4O_6(C_2H_5O)_2$ requires C = 61.01; H = 2.82 per cent.

It consisted of colourless, prismatic needles melting at $322-324^\circ$, and was identified as acetylcatellagic acid. The catellagic acid produced by the hydrolysis of this compound was characterised by the readiness with which it sublimed at high temperatures, and differed in no respect from the compound obtained by the agency of persulphates.

A study of electrolytic oxidation of *p*- and *m*-hydroxybenzoic acids gave somewhat disappointing results, and it soon became evident that the employment of persulphate for the oxidation of these acids in this

respect was much more advantageous. The subject has consequently been put on one side, but it is hoped that by employing the water-cooled anode, as in the experiments with gallic acid, a more satisfactory result may be obtained.

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CXVII.—*The Thermal Decomposition of Hydrocarbons.*
Part I.* [*Methane, Ethane, Ethylene, and*
Acetylene.]

By WILLIAM ARTHUR BONE and HUBERT FRANK COWARD.

MUCH has been written concerning the action of heat on hydrocarbons, and the separation of carbon in flames, since Dalton and William Henry conjointly studied the decomposition of methane and ethylene when subjected to the continued action of electric sparks (Dalton's "*New System*," vol. I, pp. 440, 447; *Phil. Trans.*, 1809, 99, 446). Owing, however, to the complexity of the phenomena, and the difficulty in realising conditions under which crucial evidence can be obtained, we are still far from understanding the precise modes of decomposition of even the simplest hydrocarbons, whilst the final elucidation of the question as it affects the higher members of the various series will probably tax our experimental resources to the utmost for many years to come.

That the ultimate resolution of a hydrocarbon into its elements at high temperatures cannot be regarded in general as the immediate result of a single chemical change was proved by Marchand in 1839 (*J. pr. Chem.*, 36, 478), when he obtained large quantities of methane during the decomposition of ethylene at a bright red heat. This led him to represent the initial stage of the transaction as involving the simultaneous liberation of carbon and methane as follows:



This view derived some support from the later observation of Buff and Hofmann (*Annalen*, 1860, 113, 129), that when a platinum wire is electrically heated to dull redness in ethylene, the gas is decomposed, yielding carbon and much methane without any appreciable change in volume. But the cogency of this otherwise important piece of evidence

* A preliminary notice of this investigation appeared under the names of Bone and Jordan in the *Proceedings*, 1901, 17, 164.

is weakened, as V. B. Lewes has justly remarked, by the fact that denser hydrocarbons, both solid and liquid, are undoubtedly formed from ethylene at incipient red heat.

During the years 1863—1869, Berthelot made a comprehensive study of the behaviour of hydrocarbons at high temperatures (*Ann. Chim. Phys.*, 1863, [iii], 67, 53; 1866, [iv], 9, 413, 455; 1867, [iv], 12, 5, 122; 1869, [iv], 16, 143, 148, 153, 162). He contended that a hydrocarbon is never directly resolved into its elements, but the primary change always involves either a polymerisation (for example, acetylene to benzene), or a condensation of two or more molecules to form a denser hydrocarbon with elimination of hydrogen. These denser molecules in turn undergo a series of similar changes until carbon finally appears as the result of the decomposition of an extremely complex molecular aggregation. In elaborating this idea he convinced himself that the successive changes involved in the decomposition of any particular hydrocarbon are usually either all individually reversible or may be so grouped as to comprise a series of reversible cycles, and that therefore at any given temperature there would finally be established a complex state of equilibrium between hydrogen, methane, ethane, ethylene, acetylene, benzene, styrolene, diphenyl, anthracene, naphthalene . . . and carbon.* In no case, however, was the attainment of such a state of equilibrium ever proved by any quantitative measurements; it was considered sufficient to obtain qualitative evidence of the reversibility of the principal individual reactions and to deduce the general theory by the application of first principles.

With regard to the four hydrocarbons dealt with in the present paper, Berthelot maintained that methane is primarily decomposed either into acetylene and hydrogen, or possibly into ethane and hydrogen, in accordance with one or other of the following equations:



* Berthelot's views are summarised in the following passage from one of his memoirs (*Ann. Chim. Phys.*, 1866, [iv], 9, 471). " . . . que la décomposition immédiate d'un carbure d'hydrogène ne répond pas à sa résolution en éléments, mais à sa transformation en polymères, ou en carbures plus condensés avec perte d'hydrogène. Cette transformation ne s'effectue point d'ailleurs à une température absolument fixe et comparable à celle d'ébullition d'un liquide; mais elle s'opère pendant un vaste intervalle de température compris entre le rouge sombre et le rouge blanc: durant cet intervalle le carbure est décomposé en proportion d'autant plus forte et avec une vitesse d'autant plus grande que la température est plus élevée. . . . Entre chaque genre de réaction et la réaction réciproque il s'établit fréquemment une sorte d'équilibre mobile, variable avec la température et les corps qui se trouvent en présence, équilibre analogue à celui qui se produit lors la dissociation des composés binaires."

Ethane, he considered, yields either ethylene and hydrogen, or acetylene, methane, and hydrogen, as follows :

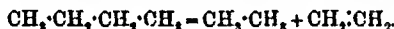


whilst ethylene yields either acetylene and hydrogen, or acetylene and ethane,



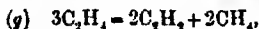
He regarded acetylene as "le produit ultime des décompositions pyrogénées . . . générateur fondamental des carbures pyrogénées." It exhibits in a high degree the power of polymerising, or of condensing with either hydrogen or aromatic hydrocarbons at high temperatures, but it is never directly resolved into its elements.

But plausible and attractive as Berthelot's theory may appear, evidence of its insufficiency was soon forthcoming. In 1873 T. E. Thorpe and J. Young, as the result of an investigation on the combined action of heat and pressure on the paraffins (*Proc. Roy. Soc.*, 21, 184), concluded that the primary decomposition gives rise to an olefine and a lower paraffin without loss of hydrogen somewhat as follows :



Moreover, in 1886, H. E. Armstrong and A. K. Miller (*Trans.*, 49, 74) drew attention to the almost complete absence of acetylene and its homologues from the products of the manufacture of oil gas from petroleum, which were found to consist largely of ethylenic and benzenoid hydrocarbons, and suggested that the latter may be derived directly from the corresponding paraffins (for example, benzene from hexane) without the intervention of acetylene.

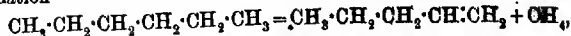
The work of V. B. Lewes, chiefly on ethylene, forms one of the most notable recent contributions to our knowledge of the subject (*Proc. Roy. Soc.*, 1894, 55, 90; 1895, 57, 394). He concluded that ethylene is primarily resolved into equal volumes of acetylene and methane as the result of the following termolecular change :



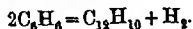
and that the acetylene subsequently either polymerises or is resolved into its elements, according to the temperature. With regard to methane, he agreed with Berthelot that it is initially transformed into acetylene and hydrogen in accordance with the equation (a).

In 1896 Haber (*Ber.*, 29, 3691) published a paper on the decomposition of the higher paraffins, in which he vigorously assailed Berthelot's views. In the case of *n*-hexane, he conclusively proved that at temperatures between 600° and 800° the primary decomposition involves the elimination of methane and the simultaneous form-

ation of one of the next lower olefines, C_5H_{10} , in accordance with the equation



a change which he regarded as typical of all the higher paraffins. In the aromatic series, on the contrary, he recognised a marked disposition to form more complex molecules with the elimination of hydrogen, for example, diphenyl from benzene:



Haber's views as to the behaviour of acetylene at high temperatures show how completely he accepted the prevailing notion of its inherent superior stability over that of all other hydrocarbons. He believed that, whilst at 600° it polymerises rapidly and at 800° yields large quantities of hydrogen, it is, nevertheless, at higher temperatures "in starker Verdünnung jedem anderen Kohlenwasserstoff an Beständigkeit überlegen." He severely criticised Lewes' work, however, and rejected the acetylene theory of the luminosity of hydrocarbon flames.

In spite of the counterbalancing weight of evidence derived from the behaviour of the higher paraffins, there has undoubtedly been a tendency during recent years to overestimate the importance of acetylene as a factor in the breaking down of hydrocarbons at high temperatures, as shown in Lewes' attempt to identify the primary formation and subsequent decomposition of acetylene as the sole cause of the luminosity of hydrocarbon flames, a doctrine which has, unfortunately, crept into many reputable text-books. But the experimental evidence on which such views have been based seems to us wholly insufficient and lacking in cogency. The detection of quite insignificant quantities of acetylene among the decomposition products in a particular experiment has far too often been put forward as satisfactory proof of its primary and predominant formation, whilst the presence of twenty times as much methane has been either altogether ignored or passed over as relatively unimportant. Moreover, whereas the influence of temperature on the nature and sequence of the changes involved has received considerable attention, the equally important factor of time has been largely disregarded. We venture to think that the facts brought to light during the present investigation will go far to determine the relative importance of methane and acetylene as high temperature decomposition products.

Several years ago, one of us, in conjunction with Dr. D. S. Jordan, proved that methane is the only hydrocarbon formed synthetically from its elements at temperatures between 1000° and 1200° (Trans., 1897, 71, 41; 1901, 79, 1042), and, although this conclusion has recently been doubted, it has been confirmed by a careful repetition of the original

experiments, and derives additional support from the results of the present research.

The range of temperature covered by our experiments extends from about 500° up to nearly 1200° , and special attention has been paid to the influence of the time factor on the various decompositions. The main conclusions, which materially differ in several important respects from those of previous workers, are summarised in the following paragraphs:

(1) Methane, which is by far the most stable of the four hydrocarbons examined, is always a principal product of the decomposition of the other three, especially at temperatures above 800° . It decomposes for the main part *directly* into carbon and hydrogen, and the process, which is probably reversible at all temperatures, is (at least within the temperature range above indicated) chiefly a surface phenomenon.* The carbon deposited from methane is of a peculiarly hard and lustrous type, wholly different from the dull, soft variety yielded by the other three hydrocarbons, except in so far as part of the latter may arise as the result of the secondary decomposition of methane.

(2) The decomposition of the other three hydrocarbons is not chiefly a surface effect, but takes place throughout the main body of the gas.

(3) Acetylene is a principal product of the decompositions of ethylene, but not of either methane or ethane. The equation put forward by V. B. Lewes for the decomposition of ethylene is, however, disproved.

(4) At comparatively low temperatures, acetylene exhibits a strong tendency to polymerise, forming benzene, &c., so that whenever acetylene is a principal primary product in the decomposition of another hydrocarbon (for example, in the case of ethylene) there is always a marked secondary formation of aromatic hydrocarbons at low temperatures. This tendency to polymerise reaches a maximum probably somewhere between 600° and 700° , after which it diminishes rapidly as the temperature rises, and is but little in evidence above 1000° .

(5) Both acetylene and ethylene exhibit a certain tendency to combine with hydrogen at low temperatures, forming ethylene and ethane, but the importance of this factor, which is never very great, diminishes as the temperature rises, and is insignificant above 1000° .

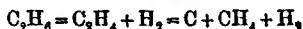
(6) One of the principal factors operative at 800° and higher

* The conclusion as to the decomposition being chiefly a surface effect applies up to 1200° , and probably at still higher temperatures, which were not investigated. Presumably at very high temperatures, decomposition would (in part at least) take place throughout the main body of the gas itself; this is certainly the case in the electric arc (Bönn and Jordan). *

temperatures is the direct "hydrogenation" of such residues as $\cdot\text{CH}_3$, $\cdot\text{CH}_2$, and possibly $\cdot\text{CH}$ (which conceivably have a momentary separate existence during the dissolution process) to methane whenever the atmosphere is already rich in hydrogen. In this and in no other way can the phenomenally large production of methane during the decomposition of the other three hydrocarbons be accounted for. The assumption of this factor also explains the greatly superior stability of methane over the other hydrocarbons at all temperatures examined.

(7) Berthelot's theory of the mechanism of hydrocarbon decomposition, with its consequent assumption of the attainment of a complex state of equilibrium at each particular temperature, is finally disproved.

(8) The mode of decomposition of any particular hydrocarbon cannot be expressed by means of a single chemical equation as ordinarily employed. For whilst it may sometimes seem possible to apply a given equation such, for instance, as

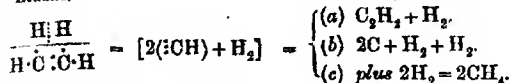
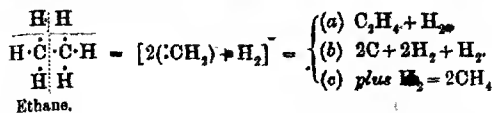


to a particular case within certain rather narrow temperature limits, any attempt to extend the system invariably results in inconsistency and confusion.

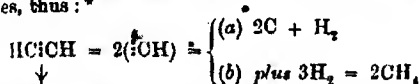
(9) But whilst the rigid application of ordinary equations is, as a rule, inadmissible, it is not difficult to formulate a scheme based on the assumption set forth in paragraph (6), showing the chief causes at work and their modes of operation in any given case. The scheme applies more particularly to ethane, ethylene, and acetylene, since the decomposition of methane is, in the main, a direct resolution of the gas into its elements.

(10) In the cases of ethane and ethylene, it may be supposed that the primary effect of high temperature is to cause an elimination of hydrogen with a simultaneous loosening or dissolution of the bond between the carbon atoms, giving rise to (in the event of dissolution) residues such as $\cdot\text{CH}_3$ and $\cdot\text{CH}_2$. These residues, which can only have a very fugitive separate existence, may subsequently either (a) form $\text{H}_3\text{C}\cdot\text{CH}_3$ and $\text{HC}\cdot\text{CH}$, as the result of encounters with other similar residues, or (b) break down directly into carbon and hydrogen, or (c) be directly "hydrogenised" to methane in an atmosphere already rich in hydrogen. These three possibilities may all be realised simultaneously in the same decomposing gas in proportions dependent on the temperature, pressure, and amount of hydrogen present. The whole process may be represented by the following scheme, the dotted line indicating the tendency to dissolve the bond between

the carbon atoms which becomes actually effective at higher temperatures.*



(11) In the case of acetylene, the main primary change may be either one of polymerisation or of dissolution, according to the temperature, and if the latter, it may be supposed that the molecule breaks down across the triple bond between the carbon atoms, giving rise to 2(:CH), and that these residues are subsequently either resolved into carbon and hydrogen or "hydrogenised," according to circumstances, thus: *



↓
Polymerisation.

Incidentally, it may be observed that the rates of decomposition of these hydrocarbons are very much slower than their rates of combustion, and that therefore in the propagation of a flame through a homogeneous mixture of a hydrocarbon and oxygen, oxidation will probably take precedence of all other chemical phenomena.

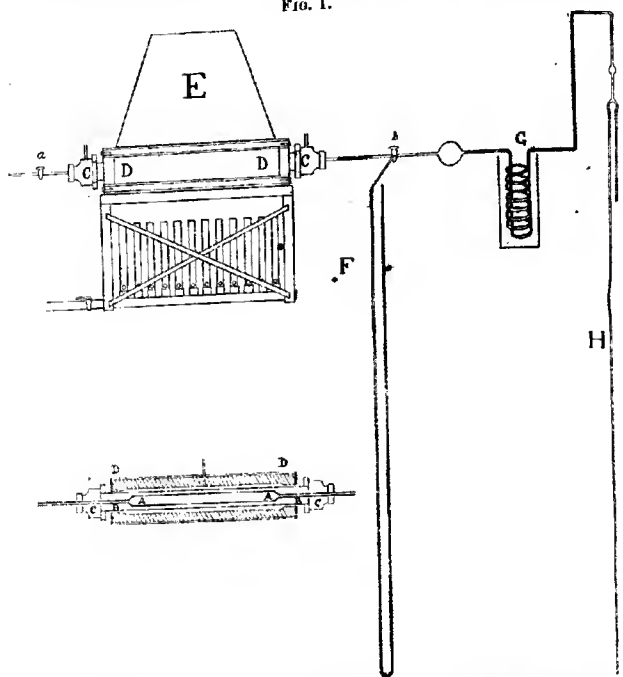
EXPERIMENTAL.

Apparatus and Methods.—The apparatus employed in the experiments above 700° consisted of an arrangement of two coaxial tubes of best Berlin porcelain, glazed within and without, similar to that used by Bone and Jerdan in their experiments on the direct union of carbon and hydrogen (*Trans.*, 1897, 71, 46), and is diagrammatically shown in Fig. 1. The inner tube, *AA* (length = 29 cm., 12 mm. internal and 16.5 mm. external diameter), terminated in narrow ends, each 16 cm. long and 2 mm. bore. It was held in position coaxially within the outer tube, *BB* (length = 50 cm., 24 mm. internal and 30 mm. external diameter), by means of two special brass end pieces, *CC*, provided with stuffing

* With regard to ethylene and acetylene, it is to be understood that changes of the kind indicated under (4) and (5), which do not involve a breaking down of the original molecule, may take place independently, but such changes are essentially low temperature effects.

boxes packed with asbestos wool moistened with "Roman" cement, which rendered the joints between the two tubes quite gas-tight. These brass end pieces were provided with side-tubes, which permitted of a slow current of pure dry hydrogen being maintained throughout the annular space between the two porcelain tubes throughout each experiment, thereby both ensuring the even heating of the inner tube and protecting its contents from any contamination with the furnace and protecting its contents from any contamination with the furnace

FIG. 1.



The tube at a leads to the drying tube and gas-holder; in circulation experiments to the large globe, &c.

gases. The tubes were heated mainly by radiation from the fireclay walls of the specially designed gas furnace (length = 35 cm.) containing thirteen powerful burners, with a draught induced by the iron chimney, *E*. The furnace was protected by means of thick screens of asbestos mill-board, and the gas supply was automatically controlled by means of a Stott governor. The temperature of the porcelain tubes was recorded by a Le Chatelier thermo-junction

connected with a dead-beat galvanometer, and it could be kept practically constant (within a total variation of about 20°) for many hours together. The narrow ends of the inner tube, *AA*, projected some distance on either side beyond the furnace; one of these ends was connected, through the stopcock, *a*, and drying tubes containing calcium chloride, with a glass holder containing the gas under investigation; the other end communicated, through the three-way stopcock, *b*, with the capillary manometer, *F*, the spiral condenser, *G* (which was externally cooled by ice during each experiment), and the automatic Sprengel pump, *H*.

At the outset of an experiment, the porcelain tubes were heated to the desired maximum temperature, and the inner tube thoroughly exhausted. The tap *b* was thereupon closed, and by opening *a* the gas under investigation was admitted until the manometer indicated a pressure slightly above that of the outside atmosphere. The gas was then maintained at the experimental temperature for a definite period of time, during which pressure records could be taken at regular intervals, and, finally, by momentarily opening the tap *b*, a sample of the residual gas was instantly drawn over into the vacuum condenser and pump connexions, whence it was afterwards collected through the pump for analysis. After removal of the sample, the whole apparatus was again exhausted in readiness for the next experiment; in this way a series of consecutive experiments at a particular selected temperature could be made without cooling down the porcelain tubes.

The presence of aromatic hydrocarbons in the products was indicated by the appearance of a mist in the bulb of the spiral condenser when the tap *b* was opened.

Whilst the above represents the usual experimental procedure, it was subject to considerable variations for special reasons. By a slight modification of the apparatus, the action of heat on a flowing stream of the gas could be investigated. Also, the length of the inner tube was sometimes varied, and occasionally a tube of the same internal diameter as the one shown in the diagram, but without narrow ends, was used, in which case each end of the tube was fitted with a ground-glass joint secured by a short length of indiarubber tubing. When the influence of hot surfaces on the decomposition of methane was to be studied, the inner tube was packed with fragments of the selected solid, but otherwise no packing was employed.

A notable departure from the usual procedure was made at temperatures below 700°, where the rate of decomposition in a particular case was slow enough to admit of the employment of the "circulation" method devised by Bone and Wheeler (*Trans.*, 1903, 83, 1076). In such a case the apparatus was converted into a closed

system by the insertion of a larger globe and a series of by-passed sampling tubes (for particulars of the arrangement see *Phil. Trans.*, 1906, *A*, 205, 9), thus rendering it possible to operate on large volumes of the gas under examination, and to follow the course of its decomposition both by pressure records and a series of gas samples cut out at regular intervals without disturbing the experimental conditions.

Analysis of the Gases.—As the gaseous products often contained acetylene, ethylene, ethane, methane, and hydrogen as well as small quantities of carbon monoxide, formed by the reduction of the surface of the inner porcelain tube by carbon deposited on it at high temperatures,* special methods were adopted for the separate estimation of each constituent. For the estimation of ethane (if any) present, a portion of the gas remaining after the complete removal of acetylene, ethylene, and carbon monoxide was subjected to the action of "oxidised" palladium sponge at 100° until all the hydrogen was eliminated; the residual saturated hydrocarbon was subsequently exploded with excess of oxygen and the ratio C/A determined in the usual manner.

In recording the composition of the gaseous products in the various experiments, any small percentage of adventitious nitrogen or of carbon monoxide has been omitted; the tabulated results therefore give the percentage composition of the nitrogen- and carbon monoxide-free products.

Experiments with Methane.

The methane was prepared by the method described by Bone and Wheeler (*Trans.*, 1902, 81, 541); the ratio C/A obtained in an explosion-analysis was exactly 2.0, showing that the gas was quite free from hydrogen.

(a) Preliminary experiments showed that the rate of decomposition is inappreciable at temperatures below 700° unless a very large surface is exposed to the gas by packing the heated tube with some porous material. In one experiment at 785° (no "packing" in the tube) the gaseous products at the end of an hour contained no less than 91.6 per cent. of methane, the remainder being hydrogen without even a trace of acetylene. None of the other hydrocarbons investigated exhibited anything like so high a stability at this temperature.

Experiments at 1000°.—Comparative experiments at this temperature, in which the heated tube was used both with and without

* It is impossible to avoid a certain amount of reduction of the porcelain by carbon at temperatures above bright red heat.

any special "packing," proved how largely the decomposition is a surface effect; indeed, we are of the opinion that it is entirely so.

(b) The following table refers to a typical series of experiments in which the gas was shut up in the heated tube (unpacked) at atmospheric pressure for periods of time varying from one to 60 minutes:

TABLE I.

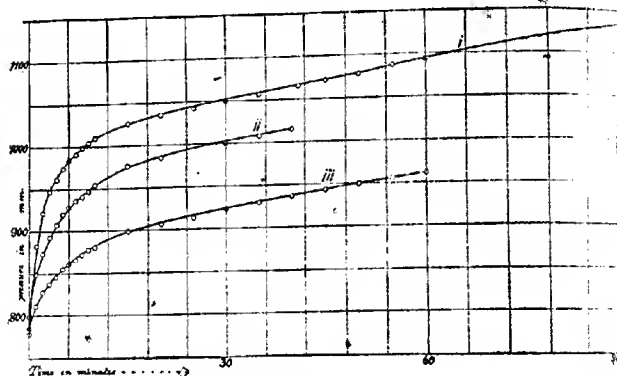
Temperature	985°.	985°.	1000°.	985°.	1015°.
Duration of heating (mins.)	1.	5.	15.	30.	60.
Percentage composition of gaseous products.					
Acetylene	0.5	0.5	nil	nil	nil
Unsaturated hydrocarbons	0.3	0.5	1.3	0.35	nil
Methane	90.4	75.4	65.25	62.85	48.2
Hydrogen	8.8	23.6	33.3	36.8	51.2

It will be observed: (1) that the rate of decomposition, for an equal amount of surface exposed to the gas, was about sixty times greater at 985° than at 785°; (2) that the formation of acetylene or unsaturated hydrocarbon could only be detected so long as the methane concentration exceeded about 60 per cent., and (3) that with lower methane concentrations the gas continued to be directly resolved into its elements in contact with the hot walls of the tube. It should be added that, in harmony with (2), only at high methane concentrations was there any indication of the formation of aromatic hydrocarbons by the appearance of a slight mist in the bulb of the cooling worm when the tap leading out of the heated tube was opened.

(c) Further insight into the general character of the phenomena is gained by a comparison of the pressure curves (Fig. 2, ordinates = pressure in mm; abscissae = time in minutes) obtained in a series of three experiments in which the gas, in the first instance undiluted, but in the two subsequent experiments diluted with either 1 or 3 vols. respectively of nitrogen, was introduced into the hot tube (unpacked) at initially nearly the same pressure. It may be remarked that in experiments of this kind it is absolutely necessary first of all to coat completely the walls of the hot tube with a layer of carbon deposited by methane in course of active decomposition, for otherwise changes in the surface conditions during an experiment would render the results valueless for comparative purposes. The curves obtained show that, especially in the case of the undiluted methane, the rate

of decomposition is during the first few minutes proportional to some high power of the concentration, but that afterwards it rapidly approaches, and finally attains, a value corresponding to a reaction of the first order. The correct interpretation of these curves is, we think, to be found in the fact that they refer to a condition of things in which highly condensed layers of gas are decomposing in contact with a hot surface. Such layers would be formed instantaneously when the gas was first introduced into the hot vacuum tube, and rapid decomposition would at once ensue; the consequent outrush of hydrogen from the surface would speedily reduce the methane concentration not only in the surface layer, but also in the main body of the gas outside, thus setting up more normal conditions

FIG. 2.



Curve I. Undiluted methane.
 " II. Methane diluted with its own volume of nitrogen.
 " III. " " " three times its own volume of nitrogen.

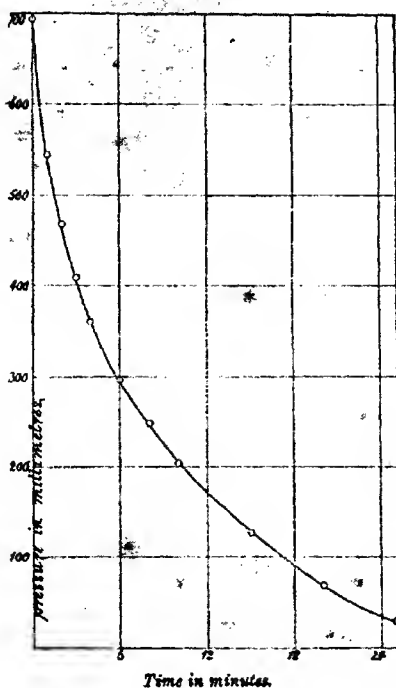
in the system. It is clear also that the formation of minute quantities of acetylene and unsaturated hydrocarbon (including benzene) is a circumstance associated with the initial "abnormal" period, the normal conditions corresponding with the direct resolution of the methane into carbon and hydrogen in contact with the hot surface.

(d) The next experiment shows the effect of largely increasing the surface exposed to the gas. The hot tube was packed with fragments of quicklime*; the decomposition now became extremely rapid, the

* The use of porous porcelain for this purpose was found to be inadmissible, owing to the readiness with which it is attacked and reduced by the methane (or possibly by the carbon deposited from methane) at this temperature. How strong this reducing action is may be gathered from the fact that in one experiment, in which the tube was packed with this material, the gases contained no less than

products containing only 1.9 per cent. of methane after twenty-five minutes, whilst at the end of an hour, when equilibrium was practically established, only 0.7 per cent. remained (temp. = 1030°). The final gases contained 2.8 per cent. of carbon monoxide, formed by the reduction of the surface exposed to the gas. The curve showing the methane concentrations during the first half of the experiment (Fig. 3, ordinates = pressure of methane in mm.; abscissae = time in

FIG. 3.



mins.) indicates a much more rapid setting up of "normal" conditions than in the previous experiments, where the surface exposed to the gas was very much smaller. After the third or fourth minute the 10.5 per cent. of carbon monoxide after 30 minutes and 22.5 per cent. after 60 minutes (nitrogen = 0.7 per cent. only). We do not know that this strong reducing action on porous porcelain has been noticed before. In similar experiments with quicklime the action was very slight, the gases containing only 2.8 per cent. of carbon monoxide after 60 minutes.

rate of decomposition assumed a value corresponding with a reaction of the first order, and this was steadily maintained until the end of the experiment. The following table gives two sets of values for the expression $1/\log C_0/C_t$, one for the whole duration of the experiment, and the other in which C_0 is taken as the methane concentration at the third minute:

TABLE II.

<i>t</i> Minutes.	<i>P</i> , Total pressure in mm.	<i>C</i> , Methane concentration in mm.	$1/\log C_0/C_t$	
0	790.0	894.0	—	—
1	942.0	543.5	0.1062	—
2	1020.5	466.5	0.0862	—
3	1080.5	408.0	0.0769	0.0582
4	1129.5	360.5	0.0711	0.0560
6	1198.0	295.0	0.0619	0.0490
8	1249.0	246.5	0.0562	0.0462
10	1296.0	203.0	0.0539	0.0452
15	1382.0	125.0	0.0500	0.0440
20	1445.5	70.0	0.0498	0.0458
25	1493.0	28.5	0.0556	0.0528

Experiments at 1150—1160°.—The following typical series of experiments, in which the gas was initially admitted to the (unpacked) tube at 1150—1160° under atmospheric pressure, afford striking proof, not only of the extraordinarily great stability of methane as compared with other hydrocarbons examined at this temperature, but also of the fact that the "normal" decomposition does not involve the formation of acetylene. For, except during the first minute, not a trace of acetylene could be detected among the products, nor was there any indication of the formation of aromatic hydrocarbons. The gas was undoubtedly resolved directly into carbon and hydrogen in contact with the hot walls of the tube. The results of this series of experiments are tabulated below:

TABLE III.

Temperature	1150°	1150°	1160°	1150—1160°
Duration of heating (mins.)	1.	5.	60.	180.
Acetylene	C.5	nil	nil	nil
Methane	44.6	27.25	22.8	9.15
Hydrogen	54.9	72.25	77.7	90.85

Character of the Carbon obtained from Methane.—The form in which the carbon was deposited from the decomposing methane at all

temperatures deserves special notice. It was entirely a surface deposit of a peculiarly hard and lustrous variety, almost metallic in appearance, and totally different from the dull, soft variety yielded by acetylene, or any of the other hydrocarbons examined under similar conditions.* This circumstance not only harmonises with the view that the decomposition of methane is, at these temperatures, a surface effect entirely, but is inconsistent with the supposition that the primary decomposition involves the formation of acetylene, for example, $2\text{CH}_4 = \text{C}_2\text{H}_2 + 3\text{H}_2$, which must now be regarded as untenable. Moreover, it seems probable that the peculiar properties of the "gas carbon" formed in the crown of the retorts during the manufacture of coal gas, as well as the characteristic metallic lustre of the coke obtained in coke-oven practice, where high temperatures prevail, are due to this "surface" decomposition of methane. The general character of the decomposition also, in a great measure, accounts for the comparatively feeble luminosity of the flame of methane.

Experiments with Ethane.

(a) *Circulation Experiments at 675°*.—After some preliminary trials, 675° was adopted as a suitable initial temperature, the apparatus being fitted with the necessary connexions for a "circulation" experiment, including a series of by-passed sampling tubes in order that samples of the gas might be shut off at intermediate periods during the experiment, without in any way altering the pressure in the apparatus or interrupting the course of chemical change. The apparatus so arranged had a capacity of about 3 litres. Pure ethane, prepared from zinc ethyl, was set circulating through the heated (unpacked) tube ($T = 675^\circ$) at an initial pressure of 248 mm.; this low pressure, together with the fact that the temperature of the hot tube was well below that at which methane begins to decompose in similar circumstances, would, it was thought, make it easier to discover the character of the primary reaction. The gas decomposed fairly rapidly, the pressure in the apparatus increasing by more than 80 per cent. within three hours, after which it remained nearly constant. In the spiral condenser, which was kept at 0° throughout the experiment, there appeared a few minute crystals of naphthalene mingled with traces of a tarry substance, but curiously enough no benzene could be detected.

Analyses of samples of the gas (see table IV. below) shut off in the by-passed tubes at intermediate points during the experiment revealed the formation of much ethylene and hydrogen, but compara-

* Except, of course, in so far as the other hydrocarbons may yield the hard variety as the result of the secondary decomposition of methane.

tively small quantities of acetylene during the initial stages, followed by a considerable accumulation of methane, at the expense of ethylene, towards the end of the process. Carbon was also deposited in the hot tube:

TABLE IV.

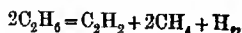
Temperature = 675°. Initial Pressure of Ethane = 248 mm.

Time (hours)	1.	1½.	3.	6.
P_2/P_1 *	1.47.	1.70.	(1.8).	1.87.
Percentage composition of gaseous products.				
$\left\{ \begin{array}{l} C_2H_2 \\ C_2H_4 \\ C_2H_6 \\ CH_4 \\ H_2 \end{array} \right.$	$\left\{ \begin{array}{l} 4.1 \\ 24.7 \\ 34.7 \\ 8.4 \\ 28.1 \end{array} \right.$	$\left\{ \begin{array}{l} 5.1 \\ 24.1 \\ 9.8 \\ 19.9 \\ 41.1 \end{array} \right.$	$\left\{ \begin{array}{l} 2.8 \\ 16.4 \\ 7.8 \\ 32.9 \\ 40.6 \end{array} \right.$	$\left\{ \begin{array}{l} 1.9 \\ 0.7 \\ 2.0 \\ 54.5 \\ 40.9 \end{array} \right.$

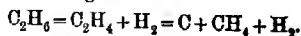
* Ratio of the pressure in the apparatus to the initial pressure.

On repeating the experiment, it was found that an initial pressure of 221 mm. (corresponding with 1.20 grams) of ethane ultimately gave rise to 207 mm. of hydrogen, 213 mm. of methane, 3 mm. of acetylene, as well as 0.4 gram (at least) of a soft, flaky variety of carbon and about 0.05 gram of almost pure naphthalene, but no benzené. At an intermediate point during the experiment, when about 86 per cent. (that is, 189 mm.) of the original ethane had disappeared, the gaseous products contained as much as 19 per cent. of ethylene.

The above facts are clearly inconsistent with Berthelot's view that the primary decomposition of ethane may be represented by the equation



or, indeed, with any other theory involving the prominence of acetylene among the initial products. On the other hand, they certainly suggest, and taken by themselves apart from any other evidence might almost seem to prove, that the sequence of changes may be represented by the following scheme:



But, as will be shown later, this cannot be considered as portraying the real mechanism of the process, although in a crude way it expresses its outward character.

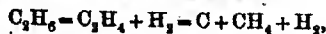
(b) *Experiments at 800°.*—(1) At this temperature ethane decomposes so rapidly that the adoption of the "circulation" method was quite out of the question. Accordingly, we had to be content with

shutting up the gas in the hot tube (unpacked) for definite periods of time, keeping a sharp look out for the appearance of any mist in the bulb of the spiral condenser when the products were finally allowed to escape out of the zone of reaction. In considering the results of the following typical series of experiments, it must be borne in mind that the rate of decomposition of methane under similar conditions was found to be negligible, except when the heating was prolonged beyond thirty minutes :

TABLE V.

Temperature	810°.	805°.	810—815°.	810°.	810—815°.
Time (mins.)	1.	5.	15.	30.	60.
Appearance in spiral condenser	Yellow mist and deposition of crystals.	White mist, no crystals.	No appearance of either mist or crystals.		
Percentage composition of gaseous products.					
$\left\{ \begin{array}{l} \text{C}_2\text{H}_2 \\ \text{C}_2\text{H}_4 \\ \text{C}_2\text{H}_6 \\ \text{CH}_4 \\ \text{H}_2 \end{array} \right.$	$\left\{ \begin{array}{l} 1.90 \\ 11.20 \\ 17.90 \\ 31.30 \\ 37.70 \end{array} \right.$	$\left\{ \begin{array}{l} 1.20 \\ 4.40 \\ 2.40 \\ 54.55 \\ 37.45 \end{array} \right.$	$\left\{ \begin{array}{l} 0.50 \\ 0.75 \\ \text{nil} \\ 64.65 \\ 34.10 \end{array} \right.$	$\left\{ \begin{array}{l} \text{trace} \\ \text{nil} \\ \text{nil} \\ 66.0 \\ 34.0 \end{array} \right.$	$\left\{ \begin{array}{l} \text{nil} \\ \text{nil} \\ \text{nil} \\ 63.75 \\ 36.25 \end{array} \right.$
Ratio CH_4/H_2 in products.	0.83	1.46	1.90	1.94	1.75

It is evident from the composition of the gases at the end of a minute, not only that ethylene is still prominent among the primary products at this temperature, but also that, whilst acetylene and aromatic hydrocarbons could be detected, they were never present in sufficiently large amounts to be regarded as really important factors. The most striking feature about these results is, however, the rapid accumulation of methane in the products; thus, the ratio of methane to hydrogen increased from 0.83 at the end of a minute to as much as 1.94 at the end of thirty minutes, during which period all other products except carbon had entirely disappeared. So high a ratio as 1.94 is obviously inconsistent with the scheme



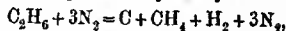
and for a long time we were quite unable to account for it. The supposition that it might be due to the secondary decomposition of aromatic hydrocarbons was at once disproved when submitted to the test of experiment. Several other possible explanations were similarly dismissed.

(2) Finally, we were compelled to look for a solution of the difficulty in some kind of change, whereby hydrogen disappears and methane is generated. A long search for such a process led to the discovery of a hitherto unsuspected and important factor in hydrocarbon decomposition, namely, the formation of methane by the direct hydrogenation of either gaseous carbon itself, or, more probably, of such residues as $\cdot\text{CH}_3$, $\cdot\text{CH}_2$, or $\cdot\text{CH}$, which may conceivably arise by the initial breaking down of a hydrocarbon molecule in an atmosphere rich in hydrogen.

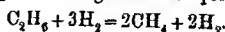
The proof that such a factor is really operative at high temperatures is furnished by the following comparative experiments on the relative amounts of methane formed when ethane, diluted to an equal degree with (a) nitrogen and (b) hydrogen, is completely decomposed under conditions precluding any sensible loss of methane. These conditions it was found were fulfilled by separately shutting up mixtures corresponding with $\text{C}_2\text{H}_6 + 3\text{N}_2$ and $\text{C}_2\text{H}_6 + 3\text{H}_2$ respectively at atmospheric pressure in the hot tube at 800° for an hour in each case. Four separate experiments were carried out with each of the two mixtures; the ethane was in all cases completely decomposed, the ultimate products consisting of carbon, hydrogen, and methane only, the percentage amounts of the last named being as follows:

Original mixture	Percentage methane obtained.				Mean.
	$\text{C}_2\text{H}_6 + 3\text{N}_2$	$\text{C}_2\text{H}_6 + 3\text{H}_2$	$\text{C}_2\text{H}_6 + 3\text{N}_2$	$\text{C}_2\text{H}_6 + 3\text{H}_2$	
1	18.5	17.15	18.3	18.7	18.15
2	42.9	38.0	48.9	40.15	41.25
3	41.25				
4	18.15				
Ratio $\frac{41.25}{18.15} = 2.27$.					

It is clear that with an inert gas, such as nitrogen, as the diluent, the ultimate result corresponded very nearly with the equation



whereas, under similar conditions with the active hydrogen, about 80 per cent. of the carbon originally present appeared as methane in the products, as though the change had been principally



This striking difference can only be attributed to the operation of a cause such as the one indicated above, and, as will be shown later, the same thing also applies in the cases of both ethylene and acetylene, the theory may be accepted as having a solid basis of fact.

(c) *Experiments at 1000° .*—At this temperature we were operating under conditions admitting of the slow decomposition of methane, so that this product rapidly accumulated at first, but afterwards diminished in amount as the heating was continued, as the following typical series of experiments indicate:

TABLE VI.—*Temperature = 1000°.*

Time (mins.)	1.	5.	30.	180.
Percentage composition of gaseous products.				
C_2H_2	2.5	0.55	0.50	0.3
C_2H_4	6.7	1.80	0.2	nil
C_2H_6	5.5	1.15	nil	nil
CH_4	32.6	41.95	37.1	25.6
H_2	52.6	54.55	61.2	74.1
Ratio CH_4/H_2	0.62	0.77	0.60	0.34

The fact that we were just able to discern the appearance of a white mist in the spiral condenser of the apparatus when the heating extended over one minute only, but none at all after five or more minutes, induced us to attempt an estimation of the amounts of aromatic hydrocarbons formed during the initial periods of the decomposition in the following special experiment.

Ten litres of ethane (13 grams) were passed through the heated tube ($T=1000^\circ$) at a speed such that each portion of the gas would not remain in the zone of reaction for longer than about half a minute. The issuing gases were passed through a weighed condenser externally cooled by ice. The amount of condensable hydrocarbons obtained did not, however, exceed 0.5 gram, or about 4 per cent. of the weight of the original ethane. This fact, together with the insignificant amounts of acetylene formed at this temperature, is clearly inconsistent with any form of "acetylene" theory, and also completely disposes of Berthelot's view that carbon arises only as the result of a long sequence of condensations in which heavy aromatic hydrocarbons play a principal rôle.

(d) *Experiments at 1140—1185°.*—Ethane is phenomenally unstable at this temperature, being scarcely able to survive a single rapid passage through the hot tube. The following results show that at the end of five minutes nothing remained besides carbon, hydrogen, and methane, the latter undergoing fairly rapid resolution into its elements. The large amount of methane at the end of five minutes is, from our point of view, a very significant feature of the decomposition:

TABLE VII.

Temperature	1140—1150°.	1150—1180°.	1175°.	1180—1185°.
Time (mins.)	5.	15.	30.	60.
Percentage composi- tion of gaseous products.	$\begin{cases} \text{C}_2\text{H}_2 \dots\dots & \text{trace} \\ \text{CH}_4 \dots\dots & 27.0 \\ \text{H}_2 \dots\dots & 73.0 \end{cases}$	$\begin{cases} \text{nil} \\ 12.75 \\ 87.25 \end{cases}$	$\begin{cases} \text{nil} \\ 10.9 \\ 89.1 \end{cases}$	$\begin{cases} \text{nil} \\ 6.0 \\ 94.0 \end{cases}$

Experiments with Ethylene.

Experiments at 570—580°.—At this temperature the gas changed slowly enough to enable us to bring the "circulation" apparatus, with its by-passed sample tubes, into operation. The initial pressure of the gas was 365 mm.; the heated tube was kept at 570° to 580°, and the gas rapidly circulated in the apparatus during two and a-half hours. The first of the intermediate samples was shut up within a few minutes of the commencement of the experiment, after about one-fourth of the original ethylene had decomposed; there was a slight fall in pressure in the apparatus as the experiment proceeded, and the course of the decomposition was marked by the expulsion of brown vapours from the hot tube. These vapours condensed, forming a viscous tar in the spiral condenser; very little carbon was deposited in the hot tube (about 0.011 gram only, or 0.75 per cent. of the weight of the carbon in the original gas). The results of the experiments will be better understood if the compositions of the gases at various periods are expressed, not in percentages as usual, but in terms of the actual partial pressures of the several constituents under constant volume, as shown on p. 1217.

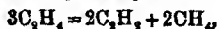
The phenomena at this temperature are evidently very complex. Acetylene, ethane, methane, hydrogen, and aromatic hydrocarbons are all produced in quantity, but the amount of carbon which actually separates is negligibly small. It is to be particularly observed (1) that whereas methane rapidly and continuously accumulated during the experiment, the hydrogen accumulated up to a certain point only (60 mins.), after which it diminished slightly; (2) that the quantity of acetylene formed exceeded that met with in the experiments upon ethane, and at the end of the first minute amounted to as much as about 12 per cent. of the gases present, and (3) that the amount of carbon in the gases progressively diminished during the experiment until finally it was just half that contained in the original ethylene,

TABLE VIII.—Temperature = 570–580°. Initial Partial Pressure of C_2H_2 = 365 mm. = 730 Units of Carbon.

Sample No.	1.	2.	3.	4.	5.	6.	7.
Time (mins.)	2.	15.	30.	45.	60.	75.	150.
Partial pressures of gaseous products in mm.							
C_2H_2	272.5	177.0	143.0	120.0	104.5	94.0	83.5
C_2H_4	43.0	28.5	20.5	22.5	26.5	31.0	23.0
C_2H_6	12.3	28.7	29.7	29.4	27.3	24.0	9.9
CH_4	16.1	54.5	67.5	77.1	90.0	95.6	132.8
H_2	17.9	72.9	93.1	101.0	102.0	97.4	93.0
Total pressure in mm...	362.5	359.0	364	361	350	342	342
Units of carbon in gases	672.7	519	454	421	406	393	365

a circumstance which indicates a continuous formation of aromatic hydrocarbons, mainly due to the polymerisation of acetylene or CH residues. In respect of (3), it is interesting to note how great is the contrast between the behaviour of ethane and ethylene at low temperatures, for whereas it was found that ethane ultimately yielded much carbon and very little aromatic hydrocarbons as it slowly decomposed at 675°, quite the reverse was observed in the case of ethylene. This difference is to be attributed to the fact that acetylene is one of the principal primary products in the decomposition of ethylene at low temperatures, whereas it is never a prominent factor in the case of ethane.

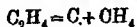
But whilst we agree with Lewes in regarding acetylene as a primary product of the decomposition of ethylene, the large accumulation of hydrogen in the above experiment *without* a corresponding separation of carbon at once disposes of his contention that the main decomposition may be represented by the equation



because, in such a case, free hydrogen could only arise by the secondary resolution of the acetylene into its elements. Moreover, during the first thirty minutes of the experiment, the rate of accumulation of methane was only about one-third of the rate of disappearance of the ethylene,* instead of two-thirds of this rate, as demanded by Lewes' equation.

* During the interval between 0 and 30 minutes, 222 mm. of ethylene disappeared, but only 67.5 mm. of methane were produced.

The experiment also proves that the equation



does not represent the main change at this temperature. This may at first sight seem inconsistent with what has been said respecting the decomposition of ethane at low temperatures, but the apparent inconsistency only emphasises the hopelessness of attempting to express the mechanism of these processes by means of ordinary chemical equations, and the necessity of regarding the phenomena from the standpoint advocated in this paper.

Experiments at 700—720°.—The results of two experiments at this temperature, with the apparatus set up in the ordinary way (that is, without the circulation arrangements), may be quoted in support of the foregoing argument, as follows:

Temperature	720°.	700°.
Time (mins.)	10.	30.
Percentage composition of gaseous products { C_2H_2	3.75	2.4
Benzene, &c.	1.25	traces
C_2H_4	63.20	27.1
C_2H_6	8.35	12.0
CH_4	20.1	37.1
H_2	3.35	21.3

Experiments at 800°.—(a) The chief interest of this series of experiments lies in the fact that the conditions precluded any appreciable decomposition of methane during the time required (fifteen minutes) to effect the disappearance of 90 per cent. of the original ethylene. There was a small increase in pressure during the first five minutes (namely, 750—790 mm.), after which it remained practically constant. The percentage compositions of the gaseous products are shown below:

TABLE IX.

Time (mins.)	1.	5.	15.	30.
Percentage composition of gaseous products. { C_2H_2	3.00	23.30	3.35	nil
C_2H_4	57.25	1.40	9.65	0.9
C_2H_6	3.25	5.00	1.80	nil
CH_4	29.40	53.40	64.45	67.7
H_2	7.10	17.00	20.75	31.4

Comparing these results with those obtained at 570°, it may be observed (1) that there was a much larger separation of carbon and a smaller formation of aromatic hydrocarbons at the higher temperature, and (2) that, whilst both acetylene and ethane were still produced, although to a less extent than at 570°, there was a much larger formation of methane, the ratio of methane to hydrogen never falling below

3.0 as compared with usually less than 1.0 at the lower temperature. This is probably due to the direct hydrogenation of such residues as CH_2 or iCH , which certainly comes prominently into play at this temperature, as the following experiments prove.

(b) In these experiments, mixtures corresponding with $\text{C}_2\text{H}_4 + 3\text{N}_2$ and $\text{C}_2\text{H}_4 + 3\text{H}_2$ respectively were separately maintained at 800° for an hour in the same apparatus, and the methane in the final products subsequently determined. The duration of the heating sufficed not only to decompose the whole of the original ethylene in each case, but also to destroy any acetylene, ethane, or aromatic products, whilst practically the whole of the methane produced would survive. The following statement as to the percentages of amounts of methane obtained in four different experiments with each of the two mixtures proves how remarkably active hydrogen is at this temperature :

	Percentage of methane found.				Mean.
	$\text{C}_2\text{H}_4 + 3\text{N}_2$	15.45, 13.7, 13.4, 12.65.....	13.8		
Original mixture {	$\text{C}_2\text{H}_4 + 3\text{H}_2$	42.6, 40.86, 44.3, 46.36.....	43.5		43.5
Ratio $\frac{43.5}{13.8} = 3.15$.					

Experiments at 950° .—At this temperature 90 per cent. of the ethylene decomposed within a minute, and scarcely any of it survived after fifteen minutes. Much carbon separated, and the production ofromatic hydrocarbons was correspondingly small. It will be observed, from the table of results given below, (1) that acetylene was detected in the products after one and five minutes, but not subsequently, and (2) that the methane/hydrogen ratio in the products never exceeded 1.65, and rapidly diminished as the experiment was prolonged, a circumstance due to the continuous secondary decomposition of the methane, which was accompanied by a steady rise in pressure in the apparatus, namely, from about 750 to 950 mm. :

TABLE X. *Temperature = 950° .*

Time (mins.)	1.	5.	15.	30.	60.
Percentage composition of gaseous products {					
C_2H_2	3.60	0.35	trace	trace	nil
C_2H_4	3.70	1.65	1.10	trace	nil
CH_4	54.75	48.35	44.76	38.20	71.9
H_2	33.10	49.65	54.15	61.80	28.1

N.B.—No ethane could be detected in the products.

An attempt was made to estimate the yield of aromatic hydrocarbons at this temperature by passing 10 litres of ethylene through

the hot tube of the apparatus at a rate corresponding with a period of one and a-half minutes' heating for each successive portion of the gas. The results showed that not more than about 4 per cent. of the gas was converted into condensable products.

Experiments at 1180°.—The following series of experiments show little else than the rapid and complete resolution of ethylene into carbon, hydrogen, and methane at this temperature. Incidentally, also, the relatively great stability of methane is again strikingly demonstrated. Moreover, as might be expected, the formation of aromatic hydrocarbons was negligibly small:

TABLE XI. *Temperature = 1180°.*

Time (mins.)	5.	15.	20.	60.	240.
Percentage composition of gaseous products.					
C_2H_2	0.50	trace	trace	trace	nil
C_2H_4	1.75	0.70	nil	nil	nil
CH_4	25.20	23.35	20.9	16.1	5.8
H_2	72.55	75.95	79.1	83.9	94.2

Experiments with Acetylene.

Experiments at 430–500°.—A "circulation" experiment proved that the principal change at this temperature is, as might be expected, one of polymerisation. The gas was circulated over a surface composed of fragments of porous porcelain contained in a short Jena glass combustion tube heated to the required temperature in a Lothar Meyer constant temperature furnace. The total capacity of the apparatus was 3550 c.c., that of the heated tube about 100 c.c., and each circuit was completed in about forty-five minutes.

Starting "all cold" with a pressure of 500 mm. of acetylene, the temperature of the furnace was slowly raised to 440° in two and a-half hours, and to 480° by the end of five hours, the pressure falling to 430 mm. during this period. The experiment was continued for fifteen hours' longer, with the following results:

Time in hours.	Temp.	Pressure mm.	Time in hours.	Temp.	Pressure mm.
0 to 5	15 to 480°	500 to 430	11	490°	308
6	491	399	12	488	295
7	493	382	14	486	270
8	492	360	16	482	249
9	493	342	17	480	243
10	492	324	20	480	213

The pressure curve, for the period five to twenty hours, is repro-

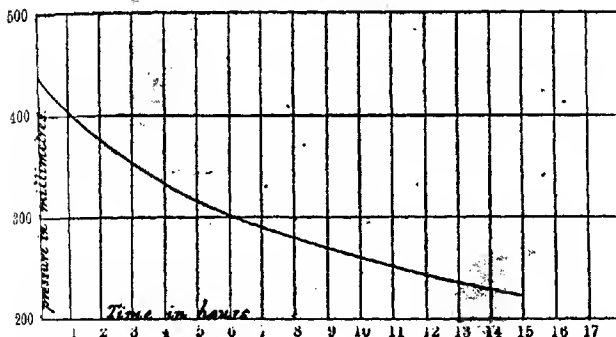
duced in Fig. 4. Analysis showed that the residual 213 mm. of gas at the end of the experiment comprised:

$C_2H_2 = 88$, $C_2H_4 = 29$, $C_2H_6 = 32$, $CH_4 = 16$, and $H_2 = 48$ mm.

It would therefore appear that of the 412 mm. of acetylene which disappeared during the experiment, about 195 mm. (or 48 per cent.) had polymerised, 160 mm. (or 39 per cent.) had decomposed into carbon and hydrogen, whilst the remaining 57 mm. had been "hydrogenised," yielding ethylene, ethane, and methane.

With regard to the "condensed" products, the whole of the porous porcelain in the heated tube was coloured dark brown or black during the experiment, and, on extraction with chloroform in a Soxhlet apparatus, tarry matter was removed, leaving the surface black by

FIG. 4.



reason of carbon impregnation. In the spiral condenser of the apparatus, which had been externally cooled with solid carbon dioxide throughout the experiment, a few drops of a limpid liquid with an aromatic odour and a green tinge had collected.

Experiments at 650°.—A similar "circulation" experiment was made at 650°. Starting with the cold reaction tube and a pressure of 510 mm., the temperature of the furnace was raised to 650° in an hour, during which the pressure fell to 330 mm. The experiment was continued for seven and a-half hours longer, at the end of which the pressure was 154 mm. Brown vapours were continuously expelled from the hot tube, and condensed in the cooled spiral. The pressure records were as follows:

Time in hours.	Temp.	Pressure mm.	Time in hours.	Temp.	Pressure mm.
0	15°	510	3	650°	200
$\frac{1}{2}$	500	475	4	643	180
1	620	353	5	642	172
$1\frac{1}{2}$	640	275	6	647	168
2	640	249	$8\frac{1}{2}$	653	154
$2\frac{1}{2}$	642	217			

The residual 154 mm. of gas comprised :

$C_2H_2 = 19$, $C_2H_4 = 15$, $C_2H_6 = 2$, $CH_4 = 45$, and $H_2 = 70$ mm.

The weight of acetylene originally charged into the apparatus was 2.59 grams (that is, 2.39 carbon, and 0.20 hydrogen). Of this, 1.56 grams (or about 60 per cent.) polymerised, 0.75 gram, or as nearly as possible 30 per cent., was resolved into carbon and hydrogen, the remaining 10 per cent. appearing as "hydrogenised" products, that is, as ethane, ethylene, and methane.

Experiments at 800°.—(1) The gas decomposed so rapidly at this temperature that the "circulation" method was abandoned in favour of the ordinary arrangement of the apparatus. Moreover, except when the gas was largely diluted with nitrogen or hydrogen, it always "flashed" as soon as it entered the hot vacuum tube, so that its temperature must momentarily have been considerably higher than was recorded by the pyrometer. The greater part of the gas was undoubtedly decomposed during this momentary "flashing," but at the end of a minute there still remained about 25 per cent. of acetylene undergoing more or less rapid change. The results of a typical series of experiments are tabulated below :

TABLE XII. *Temperature = 795°—800°.*

Time (mins.)	1.	5.	15.	60.
Percentage composition of gaseous products.				
H_2 ...	25.9	7.3	1.35	nil
C_2H_2 ...	4.2	2.7	nil	nil
C_2H_4 ...	2.65	0.7	nil	nil
C_2H_6 ...	15.00	35.3	37.65	43.0
CH_4	52.25	54.0	61.00	57.0

The appearance of a mist in the spiral condenser in the one minute experiment showed that polymerisation still occurs at this temperature, but owing to the "flashing" of the gas the conditions did not admit of any quantitative determination of the relative amount of gas so affected; it was, however, quite small, although there can be no doubt that it would have been much larger had no "flashing" occurred.

The most important feature of the above experiment is the large formation of methane, especially during the quiet decomposition

which supervened after the "flashing" had subsided, and when the atmosphere was rich in hydrogen. The fact that the final products obtained after sixty minutes contained no less than 43 per cent. of methane is difficult to explain, except on the supposition of a direct "hydrogenation" of :CH residues, formed by the initial breaking down of acetylene molecules across the triple bond between the carbon atoms.

(2) The above supposition was confirmed by a series of comparative experiments, in which mixtures corresponding with $C_2H_2 + 3N_2$ and $C_2H_2 + 3H_2$ respectively were kept in the hot tube at 800° for an hour, and the percentage of methane in the products determined. The results of four different experiments with each mixture are given below, and need no further comment:

Percentage of methane found.		Mean.
Original mixture $\left\{ \begin{array}{l} C_2H_2 + 3N_2 \dots\dots\dots \end{array} \right.$	6.9, 5.05, 5.7, 5.0.....	5.65
$\left\{ \begin{array}{l} C_2H_2 + 3H_2 \dots\dots\dots \end{array} \right.$	26.75, 25.0, 30.4, 27.2.....	27.35

(3) Some reference to the phenomenon of "flashing" may be appropriately made in this connexion. Lewes claims for acetylene the peculiar property of what may be termed "incandescent decomposition" at high temperatures, which he regards as the sole cause of the luminosity of hydrocarbon flames. Haber, on the other hand, has denied that acetylene exhibits this property, except when mixed with small quantities of oxygen. So far as our own experiments are concerned, it should be stated that, whilst entirely dissenting from the acetylene theory of luminosity, which is not at present under discussion, we agree with Lewes in regarding the luminous decomposition of acetylene at high temperatures as a property of the gas itself, and in no way dependent on the presence of oxygen.

Experiments at Higher Temperatures.—The results of numerous experiments both at 1000° and 1100 — 1150° showed that the amount of polymerisation diminished, and the direct decomposition into carbon and hydrogen increased, as the temperature was raised. But, at the same time, considerable quantities of methane still appeared in the products, and it is significant that the maximum percentage of methane always nearly coincided with the disappearance of the last traces of acetylene. The large formation of methane, which greatly exceeded the equilibrium proportions at these temperatures, must be attributed to direct "hydrogenation" of :CH residues. The results of two typical series of experiments are recorded on page 1224.

TABLE XIII. *Temperature = 1000°.*

Time (mins.)	1.	5.	60.
Percentage composition of gaseous products.			
$\left\{ \begin{array}{l} \text{C}_2\text{H}_2 \dots\dots\dots \\ \text{C}_2\text{H}_4 \dots\dots\dots \\ \text{CH}_4 \dots\dots\dots \\ \text{H}_2 \dots\dots\dots \end{array} \right.$	$\left\{ \begin{array}{l} 13.85 \\ 2.05 \\ 19.10 \\ 65.00 \end{array} \right.$	$\left\{ \begin{array}{l} 1.85 \\ 0.35 \\ 20.55 \\ 77.15 \end{array} \right.$	$\left\{ \begin{array}{l} \text{nil} \\ \text{nil} \\ 14.75 \\ 85.25 \end{array} \right.$

TABLE XIV. *Temperature = 1120–1150°.*

Time (mins.)	1.	5.	15.	75.	180.
Percentage composition of gaseous products.					
$\left\{ \begin{array}{l} \text{C}_2\text{H}_2 \dots\dots\dots \\ \text{C}_2\text{H}_4 \dots\dots\dots \\ \text{CH}_4 \dots\dots\dots \\ \text{H}_2 \dots\dots\dots \end{array} \right.$	$\left\{ \begin{array}{l} 10.0 \\ 2.0 \\ 16.0 \\ 72.0 \end{array} \right.$	$\left\{ \begin{array}{l} 0.3 \\ \text{nil} \\ 21.3 \\ 78.4 \end{array} \right.$	$\left\{ \begin{array}{l} \text{nil} \\ \text{nil} \\ 16.1 \\ 83.9 \end{array} \right.$	$\left\{ \begin{array}{l} \text{nil} \\ \text{nil} \\ 7.75 \\ 92.25 \end{array} \right.$	$\left\{ \begin{array}{l} \text{nil} \\ \text{nil} \\ 3.0 \\ 97.0 \end{array} \right.$

Comparative Experiments on the Relative Amounts of Polymerisation at Different Temperatures.

As it seemed desirable to estimate the relative amounts of polymerisation at different temperatures between 800° and 1150° under conditions calculated to eliminate as far as possible the effects of "flashing" already referred to, comparative experiments were made in the following manner. The porcelain tube of the apparatus was first of all heated to the desired temperature, and thoroughly exhausted. Acetylene was then admitted, and, as soon as the initial disturbance due to "flashing" had subsided, the pump was set working so as to draw a continuous stream of gas at a constant rate of about 4 litres per hour through the apparatus. In this way it was found that, except at the moment of the initial admission of the gas into the hot vacuum tube, no "flashing" occurred, the gas undergoing quiet decomposition as it passed through the zone of high temperature. Practically the whole of the acetylene was decomposed in each experiment; the amounts of polymerisation observed, as well as the compositions of the gaseous products, are tabulated on p. 1225. Attention is directed to the large amounts of methane formed.

TABLE XV.

Temperature	880°	1000°	1150°
v_2/v_1 *	0.68	0.66	0.77
Percentage acetylene polymerised	19.	7.5.	5.0.
Percentage composition of gaseous products.			
$\left\{ \begin{array}{l} \text{C}_2\text{H}_2 \dots\dots\dots \\ \text{C}_2\text{H}_4 \dots\dots\dots \\ \text{C}_2\text{H}_6 \dots\dots\dots \\ \text{CH}_4 \dots\dots\dots \\ \text{H}_2 \dots\dots\dots \end{array} \right.$	$\left\{ \begin{array}{l} 1.36 \\ 0.46 \\ 0.50 \\ 34.20 \\ 63.50 \end{array} \right.$	$\left\{ \begin{array}{l} 1.55 \\ 2.60 \\ \text{nil} \\ 38.00 \\ 59.65 \end{array} \right.$	$\left\{ \begin{array}{l} \text{nil} \\ \text{nil} \\ \text{nil} \\ 23.45 \\ 76.55 \end{array} \right.$

* The ratio of the volume of the gaseous products to that of the original gas.

These facts taken in conjunction with the results of the two circulation experiments at lower temperatures, indicate that the range of temperature most favourable to polymerisation lies between 600° and 700°, the tendency to this kind of change rapidly diminishes as the temperature is further raised.

The investigation is being extended to the higher members of the paraffin and other series of hydrocarbons; it is also our intention to examine further the conditions most favourable to the formation of naphthalene in these decompositions.

In conclusion we desire to express our indebtedness to the Government Grant Committee of the Royal Society for repeated grants towards the expenses of the research, and also to Dr. D. S. Jordan, for valuable aid during its initial stages.

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CXVIII.—*The Effect of Constitution on the Optical Activity of Nitrogen Compounds.*

By **REGINALD WILLIAM EVERATT, B.Sc.**

SINCE α -phenylbenzylmethylallylammonium iodide was first resolved by Pope and Peachey (*Trans.*, 1899, **75**, 1127) into dextro- and levorotatory forms in which the activity was due to the asymmetry of the quinquivalent nitrogen atom, a considerable number of substituted

ammonium iodides of the general type $abcd\text{NI}$, where $abcd$ are different alkyl groups, have been similarly resolved into their optical isomerides and their physical constants measured and tabulated.

In a paper by Miss M. B. Thomas and H. O. Jones (Trans., 1906, 89, 280), the values of the rotatory powers of ten substituted ammonium iodides were determined. These compounds formed two sets of five, all owing their activity to an asymmetric nitrogen atom attached to four alkyl groups. One set consisted of compounds containing the phenyl, methyl, and benzyl groups together with one of the following groups: ethyl, *n*- or *iso*-propyl, *isobutyl*, or *isoamyl*. The other set differed in that the benzyl group was replaced by the allyl group.

More recently, a third set has been added to these by Jones and Hill (Trans., 1908, 93, 295). This set consists of iodides containing the groups *p*-bromophenyl, methyl, and allyl together with one of the homologous groups: ethyl, *n*- or *iso*-propyl, *isobutyl*, or *isoamyl*.

The results obtained were throughout discussed with reference to the application of Guye's hypothesis to the quinevalent nitrogen atom, but it was decided that further data were necessary before deciding how far the hypothesis applied thereto.

The purpose of the present investigation was to provide further data and to render the above series more complete by preparing and resolving certain of these compounds containing the *n*-butyl group, namely, phenylmethyl-*n*-butylallylammonium iodide, *p*-bromophenylmethyl-*n*-butylallylammonium iodide, and *p*-bromophenylbenzylmethyl-*n*-butylammonium iodide. The last of these was also required for comparison with the corresponding unbrominated compound resolved by Wedekind and Fröhlich (Ber., 1907, 40, 1646). *p*-Bromophenylbenzylmethylallylammonium iodide was also prepared and resolved with a view to ascertaining its relation to the unbrominated analogue of Pope and Peachey already mentioned, and also to the remaining members of the group of brominated compounds already prepared.

The results of this investigation and their relation to those previously obtained are summarised at the conclusion of this paper. The method used for the resolution of these compounds was that of Pope and Peachey, and consisted in fractional crystallisation of the *d*-camphorsulphonate or *d*-bromocamphorsulphonate of the base from a suitable solvent. In one case, however, resolution was effected by use of *d*-tartaric and *d*-camphoric acids; the latter has not been previously used in this connexion. All measurements were made in a 2-dm. tube. In investigating the effect of temperature on the molecular rotatory power, the densities of the solutions used were taken as identical with those of water at the same temperature, whilst the values of $[M]_D$ for the acidic ions are those given by Thomas and Jones (Trans., 1906, 89, 284 *et seq.*).

Phenylmethyl-n-butylallylammonium Iodide.

Methyl-*n*-butylaniline was prepared in the manner already described by Wedekind and Fröhlich (*Ber.*, 1907, 40, 1646). The fraction collected boiled at 236—239°.

Phenylmethyl-n-butylallylammonium iodide was prepared by mixing methyl-*n*-butylaniline and allyl iodide in molecular proportions. The mixture slowly deposited crystals, and at the end of sixteen hours was quite solid and crystalline. A portion was dissolved in hot alcohol and precipitated by the cautious addition of ether. After several repetitions of this procedure, the iodide was obtained in fine colourless needles melting at 80—81° if heated rapidly:

0.245 gave 0.1722 AgI. $I = 37.98$.

$C_{14}H_{22}NI$ requires $I = 38.31$ per cent.

Phenylmethyl-n-butylallylammonium d-camphorsulphonate was prepared by boiling equivalent quantities of phenylmethyl-*n*-butylallylammonium iodide and silver *d*-camphorsulphonate with moist ethyl acetate. The silver salt was finely powdered and covered with ethyl acetate. Two or three drops of water were added, and the whole heated to boiling in a small flask over the water-bath. The substituted ammonium iodide was then added in successive small quantities, shaking well after each addition. The precipitated silver iodide was collected, and the filtrate evaporated as far as possible on the water-bath; on allowing the residue to stand in a vacuum over sulphuric acid for a few days, it became crystalline, although largely contaminated with metallic silver. Many attempts to recrystallise the salt were made; alcohol, acetone, ethyl acetate, ethylal, methylal, benzene, toluene, and other solvents being used both alone and as mixtures. In every case the camphorsulphonate separated from the solution as an oil, and a similar result followed when ether was added slowly to any of the above solutions. Hence the attempted resolution by this method was abandoned.

Phenylmethyl-n-butylallylammonium d-bromocamphorsulphonate was prepared in a similar manner from equivalent quantities of the iodide and silver *d*-bromocamphorsulphonate. After evaporating the ethyl acetate, a dark viscid mass remained, which soon became crystalline on standing in a desiccator. It was dissolved in hot acetone, but could not be obtained crystalline from this solvent. When ether was cautiously added to its solution in ethyl acetate, crystals were slowly deposited, and, after two such recrystallisations, it was found possible to recrystallise it from hot acetone.

The salt of the dextro-rotatory base was thus obtained in clusters of fine colourless needles melting, if heated rapidly, at 149—150°:

0.1825 gave 0.3731 CO_2 and 0.1174 H_2O . $\text{C} = 55.73$; $\text{H} = 7.14$.
 $\text{C}_{24}\text{H}_{26}\text{O}_4\text{NBrS}$ requires $\text{C} = 56.03$; $\text{H} = 7.07$ per cent.

The rotatory power gradually increased, and became constant after seven recrystallisations.

After seven recrystallisations, 0.1326 gram dissolved in 13.9055 grams of water gave α_D 1.34° at 14° ; hence $[\alpha]_D$ 70.3° and $[M]_D$ 361.3° .

After nine recrystallisations, 0.1264 gram in 11.1376 grams of water gave α_D 1.59° at 14° ; hence $[\alpha]_D$ 70° and $[M]_D$ 359.8° .

Hence the mean value for the basic ion at 14° is 85.6° .

The effect of temperature change on the rotatory power of the solution of the bromocamphorsulphonate was also investigated, and as usual proved to be very slight. The solution used contained 0.1674 gram of the salt in 16.2877 grams of water.

t .	α_D .	$[\alpha]_D$.	$[M]_D$.	$[M]_D$ for basic ion.
2°	1.435°	69.81°	358.8°	89.3°
11	1.44	70.06	360.1	87.1
20	1.445	70.33	361.5	84.5
30	1.45	70.82	364.0	82.0
41	1.46	71.62	368.13	82.0
50	1.47	72.36	371.9	80.9

d-Phenylmethyl-*n*-butylallylammonium iodide was precipitated from the aqueous solution of the bromocamphorsulphonate by the addition of solid potassium iodide. The iodide crystallised slowly in small prisms melting at $79-80^\circ$. After recrystallisation from cold alcohol and ether, the salt melted at 80° . A mixture of the active and inactive iodides also melted at 80° .

Determination of its rotatory power in alcohol gave the following results:

0.1692 gram in 13.2126 grams of alcohol (density of solution = 0.809) gave α_D 0.66° at 15° ; hence $[\alpha]_D$ 31.78° and $[M]_D$ 105.19° .

0.1846 gram in 12.0115 grams of alcohol (density of solution = 0.81) gave α_D 0.79° at 15° ; hence $[\alpha]_D$ 31.72° and $[M]_D$ 104.99° .

The mean value is accordingly $[M]_D$ 105.09° .

The active iodide was readily soluble in chloroform, and a determination of its rotatory power showed that it racemised rapidly in this solvent.

Thus 0.1316 gram of the iodide in 18.5623 grams of chloroform (density of solution = 1.486) gave, ten minutes after making up, α_D 0.72° at 14° ; hence $[\alpha]_D$ 34.17° and $[M]_D$ 113.1° .

After one hour, α_D 0.53° , whence $[\alpha]_D$ 25.15° and $[M]_D$ 83.25° .

„ two hours, α_D 0.38° „ $[\alpha]_D$ 18.03° „ $[M]_D$ 59.68° .

„ four „ α_D 0.21° „ $[\alpha]_D$ 9.97° „ $[M]_D$ 33° .

„ six „ α_D 0.10° „ $[\alpha]_D$ 4.75° „ $[M]_D$ 15.7° .

At the end of nine hours, the solution was found to be inactive. By extrapolation from the curve, the value of $[M]_D$ at the instant of making up the solution is 123° .

A second determination in chloroform solution was made. 0.1579 gram of iodide in 16.8748 grams of chloroform (density of solution = 1.49) gave, ten minutes after making up, α_D 0.91° at 16° ; hence $[\alpha]_D$ 33.94° and $[M]_D$ 112.1° . This solution likewise became inactive within nine hours of making up.

p-Bromophenylmethyl-n-butylallylammonium Iodide.

p-Bromophenylmethyl-n-butylallylammonium iodide was prepared by mixing allyl iodide and *p*-bromophenylmethyl-*n*-butylamine in molecular proportions. The mixture gradually deposited crystals, and, after standing for twenty-four hours, it had completely solidified to a dark red mass. This was dried on a porous plate, and a portion dissolved in alcohol and reprecipitated with ether. It then melted at $84-86^\circ$. The melting point gradually rose as this process was repeated, and finally became constant after seven recrystallisations, the value then being $105-106^\circ$, and the iodide being obtained in pure white, crystalline needles:

0.1827 gave 0.2733 CO_2 and 0.0878 H_2O . $\text{C} = 40.78$; $\text{H} = 5.33$.

$\text{C}_{14}\text{H}_{21}\text{NBrI}$ requires $\text{C} = 40.96$; $\text{H} = 5.17$ per cent.

p-Bromophenylmethyl-n-butylallylammonium-d-campfersulphonate was prepared in the usual manner by boiling molecular quantities of the above iodide and silver *d*-campfersulphonate with moist ethyl acetate. After the evaporation of the solvent, a clear gum was left. This, on standing in a desiccator, slowly became crystalline, but, although several specimens were prepared both from the crude and from the recrystallised iodide, only in one case was anything like satisfactory crystallisation attained, even when some specimens were kept for months in a vacuum over sulphuric acid. The final product was in each case a white mass, consisting of a small quantity of crystalline matter mixed with a larger quantity of gummy material. All attempts to recrystallise the material failed, although all the usual solvents, alcohol, acetone, ethyl acetate, &c., were used, both alone and as mixtures. Attempts to precipitate the salt from its solutions by adding ether or light petroleum were likewise unsuccessful. In many cases traces of crystals formed, but the amount was too small for investigation, and any attempt to increase the quantity by concentrating the solution led to the immediate deposition of an oil. This is particularly noticeable if ethyl acetate is cautiously added to the solution of the salt in benzene. The crystals deposited in this

case were shown to contain no silver, but the quantity was too small for further investigation.

p-Bromophenylmethyl-*n*-butylallylammonium *d*-bromocamphorsulphonate was prepared in a similar manner from molecular quantities of the iodide and silver *d*-bromocamphorsulphonate. The behaviour of this substance was completely analogous to that of the camphorsulphonate. It did not crystallise satisfactorily on standing, and if kept for long in a vacuum over sulphuric acid it evolved objectionable odours and seemed partly to decompose. Also, it was found impossible to recrystallise it by any method, although traces of crystals containing no silver were again obtained in one or two cases. In all the others an oil alone separated.

Since it had been shown by Miss Homer (*Proc. Camb. Phil. Soc.*, 1907, 14, 196); and by H. O. Jones (*Proc. Camb. Phil. Soc.*, 1907, 14, 376), that asymmetric nitrogen compounds can be resolved by means of tartaric acid, it was decided to try this method in the present case.

p-Bromophenylmethyl-*n*-butylallylammonium hydrogen *d*-tartrate was therefore prepared as follows. The iodide was treated in alcoholic solution with a slight excess of silver oxide, and the whole warmed and stirred. The filtrate was allowed to run into an alcoholic solution containing the molecular quantity of *d*-tartaric acid. Instead of evaporating the mixture as far as possible and then waiting for the tartrate to crystallise, the liquid was merely concentrated until it showed signs of cloudiness. A little alcohol was added until the liquid was again clear, and then ether was added until it became just turbid. The tartrate rapidly crystallised on standing, and was recrystallised very easily from alcohol and ether. After four such recrystallisations, a determination of the rotatory power was made:

0.1938 gram in 16.0582 grams of water at 15° gave $\alpha + 0.58^\circ$, whence $[\alpha]_D 24.03^\circ$ and $[M]_D 103.68^\circ$.

Taking $[M]_D$ for the ion $C_4H_4O_6H$ as 42° , from the results of Landolt on ammonium hydrogen tartrate, it is evident that the salt was resolving rapidly. Accordingly, recrystallisation by the above method was continued, the value for $[M]_D$ gradually increasing and becoming constant after eleven recrystallisations.

The salt was finally obtained in clusters of very small needles, readily soluble in water or alcohol, but only sparingly so in acetone. It melts at about 115° to a cloudy liquid, which effervesces at 141° and becomes clear. For analysis, the salt was dried over sulphuric acid in a desiccator:

0.1906 gave 0.3340 CO_2 and 0.1095 H_2O . $C = 47.8$; $H = 6.33$.

$C_{18}H_{26}O_6NBr$ requires $C = 49.96$; $H = 6.07$.

$C_{18}H_{26}O_6NBr \cdot H_2O$ requires $C = 47.97$; $H = 6.28$ per cent.

An attempt was made to estimate the percentage of water by heating the salt to 105°. The weight, however, decreased slowly, and the decrease continued indefinitely, showing that the tartrate decomposes at this temperature. A precisely similar case of a tartrate retaining water of crystallisation in alcoholic solution has been described by Jones and Hill (Trans., 1908, 83, 298).

The following determinations of rotatory power were made: After eleven recrystallisations, 0.2126 gram in 15.5070 grams of water at 16° gave α_D 0.86°, whence $[\alpha]_D$ 31.36° and $[M]_D$ 141.1°.

After fourteen recrystallisations, 0.2599 gram in 16.5416 grams of water at 15° gave α_D 0.98, whence $[\alpha]_D$ 31.19° and $[M]_D$ 140.4°.

0.2328 gram in 15.7693 grams of water gave α_D -0.92° at 15°, whence $[\alpha]_D$ 31.49 and $[M]_D$ 141.7°.

The mean value is accordingly 141.1° at 15°.

$[M]_D$ above is calculated for $C_{18}H_{26}O_6NBr \cdot H_2O$, which corresponds with $[M]_D$ for $C_{18}H_{26}O_6NBr$.

Taking $[M]_D$ for the 100 $C_4H_4O_6H$ as 42°, from the results of Landolt on ammonium hydrogen tartrate, we get $[M]_D$ for the basic ion $C_6H_4Br \cdot CH_2 \cdot C_4H_9 \cdot C_2H_5 \cdot N$ as 98°.

The effect of temperature change on the rotatory power of the solution of the tartrate was next investigated, and proved to be but small. The solution used contained 0.2303 gram of tartrate in 15.1839 grams of water. The values for the acidic ion at different temperatures are those given by Landolt:

t.	α_D	$[\alpha]_D$	$[M]_D$	$[M]_D$ for basic ion.
2°	0.94°	30.98°	139.4°	98.6°
12	0.925	30.48	137.2	95.8
20	0.91	29.99	135.0	94.25
30	0.89	29.33	132.0	89.7
42	0.87	28.68	129.1	86.1
50	0.86	28.34	127.5	84.0

The value of $[M]_D$ for the salt is, of course, $[M]_D$ for the whole molecule, including the water of crystallisation.

p-Bromophenylmethyl-*n*-butylallylanimonium iodide was slowly precipitated in clusters of needles of some size when the solutions of the above tartrate were rendered faintly alkaline with sodium carbonate solution and then treated with solid potassium iodide.

Determination of its rotatory power in alcohol gave the following results:

0.0993 gram in 9.1716 grams of alcohol (density of solution = 0.809) gave α_D 0.49°, whence $[\alpha]_D$ 27.97° and $[M]_D$ 114.7°.

0.1035 gram in 12.8905 grams of alcohol (density of solution = 0.807) gave α_D 0.36°, whence $[\alpha]_D$ 27.78° and $[M]_D$ 113.9°.

The mean value is accordingly 114.3° at 15°.

The active iodide is but sparingly soluble in chloroform. Determination of its rotatory power in this solvent gave the following results:

0.0786 gram in 16.7587 grams of chloroform (density of solution = 1.492) gave α_D 0.62° , whence $[\alpha]_D$ 44.36° and $[M]_D$ 181.9° .

This measurement was taken at 14° twenty minutes after making up the solution. After one hour, α_D 0.59° ; after two hours, α_D 0.53° ; after four hours, α_D 0.45° ; after six hours, α_D 0.37° ; after nine hours, α_D 0.25° . At the end of sixteen hours, the solution was inactive.

0.1314 gram in 18.2003 grams of solvent (density of solution = 1.495) gave α_D 0.95° , whence $[\alpha]_D$ 44.01° and $[M]_D$ 180.4° .

This solution likewise became inactive within sixteen hours. By extrapolation from the curve, the value of $[M]_D$ at the instant of making up the solution is 187.9° .

Since it had been shown that weak acids are available for the resolution of nitrogen compounds, it was decided, after the failure with *d*-camphorsulphonic and *d*-hromocamphorsulphonic acids, to try *d*-camphoric acid in this case.

p-Bromophenylmethyl-*n*-butylalkylammonium *d*-Camphorate.—An attempt to resolve the iodide by means of this compound was made simultaneously with the above work on the tartrate. The camphorate was prepared by dissolving the iodide in alcohol and treating with a slight excess of moist silver oxide, the whole being warmed and agitated thoroughly. The mixture was then filtered into an alcoholic solution containing the calculated molecular quantity of camphoric acid. The resulting clear solution was evaporated, as far as possible, on the water-bath, a milky liquid containing a little metallic silver being thus obtained. After standing for a few hours, a white, granular solid was deposited in considerable quantity. This was separated from the oily residue and dried on a porous plate. It was crystallised by precipitation from its alcoholic solution by means of ether, when it separated in beautiful silky needles melting at $147-148^\circ$:

0.2183 gave 0.4772 CO_2 and 0.1521 H_2O . $\text{C} = 59.84$; $\text{H} = 7.74$.

$\text{C}_{24}\text{H}_{39}\text{O}_4\text{NBr}$ requires $\text{C} = 59.91$; $\text{H} = 7.54$ per cent.

The rotatory power continued to decrease, and became constant after eleven recrystallisations: 0.1523 grams in 16.7965 gram of water gave α_D -0.13° , whence $[\alpha]_D$ -7.17° and $[M]_D$ -34.6° . After thirteen recrystallisations, 0.1224 gram in 16.1218 grams of water gave α_D -0.11° , whence $[\alpha]_D$ -7.24° and $[M]_D$ -34.9° .

0.1973 gram in 15.5198 grams of water gave α_D -0.18° , whence $[\alpha]_D$ -7.08° and $[M]_D$ -34.1° .

The mean value for the camphorate is accordingly 34.5° . The value

of the acid camphoric ion $C_{10}H_{14}O_4H^-$ has not previously been determined, and accordingly the sodium, potassium, and hydrogen camphorates were prepared by treating a known weight of the acid with an equivalent amount of the base and making up the solution to a known weight. From these figures, the weights of acid camphorate and water present are easily calculated, and hence $[M]_D$ for the salt determined as usual. In the case of the potassium hydrogen camphorate:

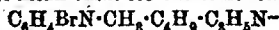
1.0437 grams in 110.4835 grams of water gave α_D 0.59° , whence $[\alpha]_D$ 25.95° and $[M]_D$ 61.7° .

1.2116 grams in 113.9712 grams of water gave α_D 0.55° , whence $[\alpha]_D$ 25.87° and $[M]_D$ 61.6° .

In the case of the sodium hydrogen camphorate:

1.0858 gram in 101.1381 grams of water gave α_D 0.59° , whence $[\alpha]_D$ 27.48° and $[M]_D$ 61° .

Hence the mean value for the ion $C_{10}H_{14}O_4H^-$ is 61.4° at $15-18^\circ$, and consequently the mean value for the basic ion



is $-(61.1^\circ + 34.5^\circ) = -95.9^\circ$.

The effect of temperature on the solution of the potassium hydrogen camphorate was examined, but, owing to the small temperature effect and the sparing solubility of the salts, which precluded the use of solutions stronger than the above, the results obtained were of little value, the differences produced over a range of 30° being within the limits of experimental error.

The above result is of some importance, inasmuch as it is the first occasion on which the resolution of one of these substituted ammonium iodides has been accomplished by more than one method. Moreover, it is the first occasion on which camphoric acid has been made use of in this connexion.

p-Bromophenylbenzylmethyl-n-butylammonium Iodide.

p-Bromophenylmethyl-n-butylamine was prepared by the interaction of molecular proportions of bromine and methyl-*n*-butylaniline in acetic acid solution. The acetic acid was then evaporated over the water-bath, and the gummy residue treated with aqueous potassium hydroxide. The base separated as a dark heavy oil, and was collected, washed, and dried over solid potassium hydroxide. It was then distilled, the fraction boiling at $177-181^\circ/18-20$ mm. being collected separately. The amine was thus obtained as a pale yellow oil. It did not give a crystalline platinichloride when treated with platinum tetrachloride and hydrochloric acid, a few drops of oil alone settling on standing.

p-Bromophenyldimethyl-n-butylammonium iodide was prepared by

mixing molecular proportions of the base and methyl iodide. A yellow solid gradually crystallised, which, after recrystallisation from alcohol and acetone, melted at 155–156°:

0.1723 gave 0.2353 CO_2 and 0.0782 H_2O . $\text{C} = 37.26$; $\text{H} = 5.05$.

$\text{C}_{12}\text{H}_{19}\text{NBrI}$ requires $\text{C} = 37.49$; $\text{H} = 4.99$ per cent.

The bromine in the amine is in the para-position, since, on heating the above iodide in a sealed tube with excess of methyl iodide, *p*-bromophenyltrimethylammonium iodide, melting at 200°, was obtained, the method being that of Hill (*Proc. Camb. Phil. Soc.*, 1907, 14, 351).

p-Bromophenylbenzylmethyl-*n*-butylammonium iodide was prepared by mixing benzyl iodide and *p*-bromophenylmethyl-*n*-butylamine in molecular proportions and allowing to stand. At the end of twenty hours, the mixture had become crystalline and semi-solid. A portion of the dark red mass was dissolved in hot alcohol, and precipitated by the cautious addition of ether. The resulting product was bright yellow, and melted indefinitely between 117° and 121°. After three such recrystallisations, the iodide was obtained as a pure white, crystalline powder, melting at 135–136° if heated rapidly. Further recrystallisation did not affect the melting point:

0.2357 gave 0.4524 CO_2 and 0.1089 H_2O . $\text{C} = 52.34$; $\text{H} = 5.14$.

$\text{C}_{18}\text{H}_{28}\text{NBrI}$ requires $\text{C} = 52.68$; $\text{H} = 5.08$ per cent.

p-Bromophenylbenzylmethyl-*n*-butylammonium *d*-bromocamphorsulphonate was prepared in the usual manner by the interaction of molecular proportions of the above iodide and silver *d*-bromocamphorsulphonate. The iodide used in this preparation was not purified by previous recrystallisation. After evaporation of the solvent, a clear dark red gum remained, which did not crystallise on standing for some months. Although several specimens of this substance were prepared, none was ever obtained crystalline, or could be induced to crystallise by any method.

p-Bromophenylbenzylmethyl-*n*-butylammonium *d*-camphorsulphonate was therefore prepared similarly by the interaction of the iodide and silver *d*-camphorsulphonate. The various specimens of this substance prepared, showed wide variation in their readiness to crystallise on standing after the solvent had been removed. Some became crystalline in a few minutes, whilst others did not, no matter how treated. The latter slowly changed to green, amorphous, sticky masses with a very unpleasant odour. The purity of the iodide was found greatly to influence the readiness to crystallise. The crystalline specimens of camphorsulphonate, whilst not crystallising from most solvents and mixtures of such, were easily obtained in the crystalline form by solution in a mixture of toluene and a little acetone, with subsequent

concentration over sulphuric acid. The crystals so formed were readily recrystallised by solution in hot acetone and subsequent addition of ether. As finally obtained, the salt formed beautiful silvery plates, very sparingly soluble in acetone, and melting, if heated rapidly, at $174-175^{\circ}$.

0.1730 gave 0.5762 CO_2 and 0.1081 H_2O . $\text{C} = 59.31$; $\text{H} = 6.94$.

$\text{C}_{23}\text{H}_{25}\text{O}_2\text{NBaS}$ requires $\text{C} = 59.53$; $\text{H} = 6.80$ per cent.

The rotatory power gradually diminished on recrystallising, and became constant after crystallising eight times as above.

After eight recrystallisations, 0.1714 gram in 11.4932 grams of water gave $\alpha_D - 1.37^{\circ}$ at 15° , whence $[\alpha]_D - 45.93^{\circ}$ and $[M]_D - 259^{\circ}$.

After eleven recrystallisations, 0.1876 gram in 17.0068 grams of water gave $\alpha_D - 1.01^{\circ}$ at 15° , whence $[\alpha]_D - 45.78^{\circ}$ and $[M]_D - 258.2^{\circ}$.

0.2442 gram in 12.8178 grams of water gave $\alpha_D - 1.75^{\circ}$ at 15° , whence $[\alpha]_D - 45.90^{\circ}$ and $[M]_D - 258.87^{\circ}$.

Hence the mean value for the camphorsulphonate is -258.7° , and the mean value for the basic ion $-(258.7^{\circ} + 50.7^{\circ}) = -309.4^{\circ}$.

The effect of temperature change on the rotatory power of the solution of the camphorsulphonate was also investigated, and as usual was found to be comparatively small. The solution used in this experiment contained 0.1876 gram of the camphorsulphonate in 17.0068 grams of water.

t	α_D	$[\alpha]_D$	$[M]_D$	$[M]_D$ for basic ion.
2°	-1.02°	-46.28°	-260.7°	-308.7°
10	1.01	45.78	258.2	307.7
20	0.99	44.94	253.4	305.0
30	0.97	44.14	248.9	302.5
40	0.95	43.37	244.6	300.2
50	0.93	42.65	240.5	298.1

p-Bromophenylbenzylmethyl-*n*-butylammonium iodide was prepared by the addition of a little solid potassium iodide to the aqueous solution of the camphorsulphonate. The iodide rapidly crystallised, and was collected, washed, and dried. It was thus obtained as a pure white solid, melting, if heated rapidly, at $137-138^{\circ}$. Recrystallisation from cold alcohol and ether left this unchanged; a mixture of the active and inactive iodides melted at $134-135^{\circ}$.

Determination of its rotatory power in alcoholic solution gave the following results:

0.1053 gram in 11.1501 grams of alcohol (density of solution = 0.81) gave $\alpha_D - 1.18^{\circ}$ at 15° , whence $[\alpha]_D - 77.13^{\circ}$ and $[M]_D - 354.8$.

0.1172 gram in 13.2110 grams of alcohol (density of solution = 0.799) gave $\alpha_D - 1.09^{\circ}$ at 14° , whence $[\alpha]_D - 76.89^{\circ}$ and $[M]_D - 353.7^{\circ}$.

Determination of its rotatory power in chloroform solution gave the following results:

0.1145 gram in 17.95 grams of chloroform (density of solution = 1.497) gave $\alpha_D -1.92^\circ$ ten minutes after making up, whence $[\alpha]_D -100.5^\circ$ and $[M]_D -462.3^\circ$; after one hour, $\alpha_D -1.32^\circ$; after two hours, $\alpha_D -0.99^\circ$; after four hours, $\alpha_D -0.51^\circ$; after six hours, $\alpha_D -0.29^\circ$; after nine hours the solution was inactive.

A second determination taken within ten minutes of making up the solution gave $\alpha_D -1.46^\circ$ for 6.0937 gram in 12.25 grams of chloroform (density of solution = 1.495), whence $[\alpha]_D -100.2^\circ$ and $[M]_D -460.9^\circ$. This solution also became inactive within nine hours.

By extrapolation from the curve, the value of $[M]_D$ at the instant of making up the solution is 481.5° .

p-Bromophenylbenzylmethylallylammonium Iodide.

p-Bromophenylbenzylmethylamine was prepared by the interaction of molecular quantities of benzylmethylaniline and bromine in acetic acid solution. The acetic acid was then evaporated over the water-bath, and the base liberated as a dark oil from the gummy residue by the action of aqueous potassium hydroxide. This was washed and separated, but solidified almost immediately. It was accordingly dissolved in ether, and the solution dried over solid potassium hydroxide, the ether being then evaporated and the residue distilled. The fraction passing over at $218-220^\circ/8-9$ mm. was collected separately; it was nearly colourless, and crystallised slowly on standing.

The base forms large, prismatic crystals, very soluble in ether, but insoluble in light petroleum. It is moderately soluble in alcohol, and is readily recrystallised from this solvent. The melting point is about 25° .

0.3165 gave 0.707 CO_2 and 0.1420 H_2O . C = 60.92; H = 4.99.

0.2449 „ 0.5465 CO_2 „ 0.1105 H_2O . C = 60.86; H = 5.01.

$\text{C}_{14}\text{H}_{14}\text{NBr}$ requires C = 60.83; H = 5.12 per cent.

The bromine in this amine is in the *para*-position, since, on heating it with methyl iodide in a sealed tube at 100° , *p*-bromophenyltrimethylammonium iodide, melting at 200° , is produced. The amine does not yield a crystalline platinumchloride on treatment with platinum tetrachloride and hydrochloric acid.

p-Bromophenylbenzylmethylallylammonium iodide was prepared by mixing allyl iodide and *p*-bromophenylbenzylmethylamine in molecular proportions. On standing, a crystalline solid and a very viscous, dark red liquid formed. It was found impossible to solidify the liquid

by any means, and accordingly it was not used in any of the succeeding experiments. The solid form was dried on a porous plate in a vacuum, and a portion was recrystallised from hot alcohol by the cautious addition of ether. After two such recrystallisations, the melting point became constant at $133-134^{\circ}$, the iodide then being obtained in beautiful iridescent laminae:

0.2103 gave 0.3527 CO_2 and 0.0846 H_2O . $\text{C} = 45.74$; $\text{H} = 4.51$.

$\text{C}_{17}\text{H}_{19}\text{NBuF}$ requires $\text{C} = 45.94$; $\text{H} = 4.32$ per cent.

p-Bromophenylbenzylmethylallylammonium *d*-bromocamphorsulphonate was prepared in the usual manner from molecular quantities of the silver salt and the substituted ammonium iodide. After evaporating the excess of solvent, the solid residue slowly became crystalline. It was found to be capable of recrystallisation if ether was very cautiously added to its acetone solution. The product so obtained was inclined to be somewhat indefinite in crystalline structure at first, but, after two or three recrystallisations, this was no longer the case. After five such recrystallisations, it melted at $137-138^{\circ}$, and a determination of its rotatory power gave the following result:

0.1414 gram in 13.2963 grams of water gave α_D 0.91° , whence $[\alpha]_D$ 42.7° and $[\text{M}]_D$ 268.2° .

The rotatory power of the bromocamphorsulphonate ion being about 275° , it follows that slight resolution has occurred, the levo-form of the base separating. This result was confirmed by precipitating the substituted ammonium iodide from the above solution by the addition of solid potassium iodide, when its solution in alcohol was found to be slightly levorotatory.

p-Bromophenylbenzylmethylallylammonium *d*-Camphorsulphonate.—Owing to the slow resolution of the bromocamphorsulphonate, the corresponding camphorsulphonate was prepared in a similar manner by the interaction of silver *d*-camphorsulphonate and the ammonium iodide. The residue, after the excess of solvent had been evaporated, crystallised rapidly. By adding light petroleum to its acetone solution and then slowly absorbing the acetone by means of sulphuric acid, it was easily recrystallised, and, after four repetitions of this process, a determination showed that resolution was effected far more rapidly than in the former case:

0.1489 gram in 13.0188 grams of water at 15° gave α_D -0.04 , whence $[\alpha]_D$ -1.735° and $[\text{M}]_D$ -9.5° .

As resolution proceeded the solubility of the camphorsulphonate in acetone rapidly diminished, and a mixture of acetone and ethyl acetate was used as solvent. The use of alcohol instead of ethyl acetate in this connexion seemed to favour the separation of the dextro-form

of the base, the value of $[M]_D$ diminishing and becoming markedly positive.

After twenty recrystallisations from the above mixture, the rotatory power became constant, and the salt was obtained in needles melting at 169° :

0.1729 gave 0.3725 CO_2 and 0.0999 H_2O . $\text{O} = 58.7\%$, $\text{H} = 6.42\%$.

$\text{C}_{27}\text{H}_{34}\text{O}_4\text{NBrS}$ requires $\text{C} = 59.08$; $\text{H} = 6.36$ per cent.

The following determinations of rotatory power were made:

• After twenty recrystallisations, 0.1819 gram in 12.141 grams of water at 16° gave $\alpha_D = -0.76^\circ$, whence $[\alpha]_D = -25.55^\circ$ and $[M]_D = -140.01^\circ$.

After twenty-three recrystallisations, 0.1324 gram in 13.9716 grams of water at 15° gave $\alpha_D = -0.49^\circ$, whence $[\alpha]_D = -35.85^\circ$ and $[M]_D = -141.65^\circ$.

0.1774 gram in 12.7911 grams of water at 15° gave $\alpha_D = -0.71^\circ$, whence $[\alpha]_D = -25.59^\circ$ and $[M]_D = -140.2^\circ$.

Hence the mean value for the basic ion at 15° is $-(140.6^\circ + 50.6^\circ) = -191.13^\circ$.

The effect of change of temperature on the rotatory power of the solution of the camphorsulphonate was next investigated, with the following results. The solution used contained 0.1791 gram of salt in 16.9945 grams of water:

t.	α_D	$[\alpha]_D$	$[M]_D$	$[M]_D$ for basic ion.
2°	-0.56°	-26.48°	-145.1°	-193.1°
10	0.55	25.01	142.5	192.0
18	0.53	25.08	137.4	189.0
31	0.50	23.73	130.0	183.6
40	0.49	23.34	127.2	183.5
50	0.47	22.49	123.2	180.8

p-Bromophenylbenzylmethylalkylammonium iodide was slowly precipitated from the aqueous solution of the camphorsulphonate by the addition of solid potassium iodide. The crystals separating were washed and dried, and then melted at $134-135^\circ$. Recrystallisation from cold alcohol did not alter this, and a mixture of the active and inactive iodides melted at 134° . Determinations of its rotatory power were made in alcohol and in chloroform solutions:

0.1246 gram in 10.4191 grams of alcohol at 15° (density of solution = 0.81) gave $\alpha_D = -1.04^\circ$, whence $[\alpha]_D = -53.68^\circ$ and $[M]_D = -240.5^\circ$.

0.0991 gram in 10.2236 grams of alcohol at 14° (density of solution = 0.808) gave $\alpha_D = -0.86^\circ$, whence $[\alpha]_D = -54.9^\circ$ and $[M]_D = -243.7^\circ$.

0.0912 gram in 17.3176 grams of chloroform at 15° gave (fifteen minutes after making up) $\alpha_D = -1.12^\circ$, whence $[\alpha]_D = -71.37^\circ$ and $[M]_D = -316.9^\circ$; after one hour, $\alpha_D = -1.56^\circ$; after two hours, $\alpha_D = -1.3^\circ$; after three hours, $\alpha_D = -1.07^\circ$ after four hours, $\alpha_D = -0.95^\circ$;

after six hours $\alpha_D = -0.78^\circ$; after nine hours, $\alpha_D = -0.55^\circ$. At the expiration of twenty-four hours the solution was quite inactive.

0.1424 gram in 16.8102 grams of chloroform at 15° (density of solution = 1.486) gave $\alpha_D = +31^\circ$ ten minutes after making up solution; hence $[\alpha]_D = 72^\circ$ and $[M]_D = 819.7$. This solution was also quite inactive after standing for twenty-four hours. By extrapolation from the curve, the value of $[\alpha]_D$ at the instant of making up the solution was -346° .

The results obtained are summarised in the following table:

M. p. of active iodide.	M. p. of <i>d</i> -camphor-sulphonate.	M. p. of <i>d</i> -bromo-camphor-sulphonate.	$[M]_D$ of ion at 15° .	$[M]_D$ of iodide in alcohol.	$[M]_D$ of iodide in chloroform solution.	Time required for complete racemisation of chloroform solution.
$\text{PhMe}(\text{C}_6\text{H}_5)(\text{C}_2\text{H}_5)\text{NI}:$						
30°		149–180°	85.6°	105.1°	123.0°	9 hours
$\text{C}_6\text{H}_5\text{Br} \cdot \text{Me}(\text{C}_6\text{H}_5)(\text{C}_2\text{H}_5)\text{NI}:$						
126	—	—	98.0	114.3	187.9	16 "
$\text{C}_6\text{H}_5\text{Br} \cdot \text{Me}(\text{C}_6\text{H}_5)(\text{CH}_3)\text{NI}:$						
137	174–175°	—	309.4	354.2	481.5	9 "
$\text{C}_6\text{H}_5\text{Br} \cdot \text{Me}(\text{C}_6\text{H}_5)(\text{C}_2\text{H}_5)\text{NI}:$						
134–135°	169	137–138	191.1	242.1	346.0	24 "

In all cases previously recorded, the value of $[M]_D$ for the iodide is greater in chloroform than in alcohol solution, and the former solution soon becomes inactive, owing to racemisation. This relation holds for the above compounds also. The value of $[M]_D$ for the iodide in alcohol is in each case greater than that of the basic ion in water; again a relation to which practically no exception is known.

The influence of temperature on the rotatory power of the ion in aqueous solution is uniform and of the usual linear type, the diagrams obtained being in every way similar to those previously published (*loc. cit.*). As usual, the effect is comparatively slight, being greatest by far in the case of the allyl member of the brominated series, where it is about 15 per cent. The melting point of the resolved iodide and of the inactive compound were in each case practically identical, and both compounds showed the usual property of melting at a temperature appreciably below their true melting point if heated slowly.

The following table brings out the chief relationships observed between the values of $[M]_D$ for the ions containing the groups mentioned:

	<i>n</i> -Butyl		<i>iso</i> -Butyl	
	Allyl.	Benzyl.	Allyl.	Benzyl.
Phenylmethyl	85.6°	253.9° (Wedekind)	55° (Thomas and Jones)	323° (Thomas and Jones)
<i>p</i> -Bromophenylmethyl ...	93.0	309.4 (Thomas and Jones)	86° (Thomas and Jones)	—
Phenylbenzylmethylallyl	—	166° (Pope and Gledhill)	—	—
<i>p</i> -Bromophenylbenzylmethylallyl ...	—	181°	—	—

It will be seen from this that the relation found in the allyl series by Jones and Hill (Trans., 1908, 93, 295 *et seq.*), that the brominated compound has a higher molecular rotatory power than the corresponding unbrominated compound, holds good in all the above cases. In the case of the corresponding *n*-butyl and *iso*-butyl compounds, no general relation is shown. In one of the above cases, the values are nearly identical, whilst in the remaining two cases they differ widely.

The compounds described in this paper show, however, one marked difference from the majority of those previously examined. It has been stated above that the solution of the active iodide in chloroform rapidly becomes inactive owing to racemisation. The time required for complete loss of optical activity is usually, at least, thirty-six to forty-eight hours, and sometimes considerably more. The *n*-butyl compounds require far less time than this, as will be seen from the table. Only one case of similar rapidity has been previously noted, namely, *p*-phenylbenzylmethylisobutylammonium iodide, which requires only seven hours. The *p*-bromophenylbenzylmethylallylammonium iodide is also more rapid than usual, requiring only twenty-four hours for complete racemisation.

The relation between the values of the molecular rotatory powers of the ions and the values of the product of asymmetry for the asymmetric nitrogen atom or ion may now be discussed.

The formula for the product of asymmetry, p'' , in terms of the molecular weights or "masses" of the four alkyl groups a, b, c, d producing asymmetry has been shown (Thomas and Jones, *loc. cit.*, 308) to be:

$$p'' = \frac{\{(a+d) - (b+c)\} \{(a+b) - (c+d)\} (a-c)(b-d)}{(a+b+c+d)^2}$$

whilst it has been pointed out that there are three possible values of p'' , corresponding to the three possible configurations:



In the case of the phenylmethyl-*n*-butylallylammonium iodide, the values are as below, those of the corresponding *iso*-butyl and *n*-propyl

compounds being appended for purposes of comparison. The values are those given by Thomas and Jones (*loc. cit.*)

Phenylmethylallyl Series: $a = C_6H_5(77)$, $b = CH_3(15)$, $c = C_7H_7(91)$.

	$[M]_D$ for basic ion.	I. $p'' \times 10^3$	II. $p'' \times 10^3$	III. $p'' \times 10^3$
<i>n</i> -Butyl	85.6°	+0.54°	+0.11°	+2.73°
<i>n</i> -Propyl	108.5	-0.59	-0.44	-0.5
<i>iso</i> -Butyl	55.0	+0.54	+0.11	+2.73

To the *p*-bromophenylmethylallyl series (Trans., 1908, 93, 308) the *n*-butyl and *isobutyl* members have been added:

$a = C_6H_4Br(156)$, $b = CH_3(15)$, $c = C_7H_7(41)$.

	$[M]_D$ for basic ion.	I. $p'' \times 10^3$	II. $p'' \times 10^3$	III. $p'' \times 10^3$
<i>n</i> -Butyl	98°	-10.59	-4.49	+8.46
<i>iso</i> -Butyl	98			
<i>n</i> -Propyl	141			

The *n*-butyl member may, however, be more appropriately compared with the values of Pope and Peachey's similar, but unbrominated, analogue (Trans., 1899, 75, 1127):

$a = C_6H_5$ or C_6H_4Br , $b = CH_3$, $c = C_7H_7$, $d = C_7H_7$.

	$[M]_D$ for basic ion.	I. $p'' \times 10^3$	II. $p'' \times 10^3$	III. $p'' \times 10^3$
Brominated	191.1°	-7.73°	-0.71	+14.6
Unbrominated	167.0	-0.07	+4.87	-1.86

In the case of *p*-bromophenylmethyl-*n*-butylallylammonium iodide, the only available comparison is with Wedekind's similar, but unbrominated, compound:

$a = C_6H_4Br$ or C_6H_5 , $b = CH_3$, $c = C_7H_7$, $d = C_4H_9$.

	$[M]_D$ for basic ion.	I. $p'' \times 10^3$	II. $p'' \times 10^3$	III. $p'' \times 10^3$
Brominated	309.4°	-2.92	+5.37	-0.66
Unbrominated	253.0	-0.28	+2.46	-1.71

A glance at the above figures suffices to show that there is no simple relation between the values of p'' and $[M]_D$ for the ion. By no arbitrary assumption as to the configuration to be assigned to given compounds can this difficulty be overcome. The only approach to regularity lies in the last two tables above, where the value of $[M]_D$ for the ion is greater for the brominated than for the unbrominated compound, whilst the value of p'' is also greater if we assign to both compounds configuration I or III in the first table and I or II in the second table.

The almost identical values of the *n*- and *iso*-butyl compounds of the *p*-bromophenylmethylalyl series is worthy of note. A similar case is found in the *n*- and *iso*-propyl compounds of the corresponding unbrominated series.

The writer desires to express his thanks to Mr. H. G. Orton for his kind interest and advice throughout this investigation.

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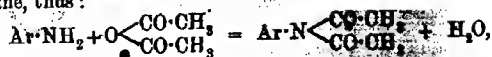
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CXIX.—*Acids as Accelerators in the Acetylation of Amino-groups.*

By ALICE EMILY SMITH and KENNEDY JOSEPH PREECE ORTON.

DI-*o*-SUBSTITUTED anilines are notoriously difficult to monoacetylate by means of acetic anhydride if the two ortho-placed atoms or groups are of negative character. Remmers (*Ber.*, 1874, 7, 350), who investigated systematically the effect of the constitution of the aniline on the rapidity and readiness of acetylation, ascertained that of negative substituents the nitro-group more effectually prevents acetylation than the halogens. Boiling or heating these anilines under pressure with acetic anhydride leads to the formation of a di-, but not of a mono-acetyl derivative (Remmers, *loc. cit.*; Ulfers and von Janson, *Ber.*, 1894, 27, 93; Sudborough, *Trans.*, 1901, 79, 532; Orton, *Trans.*, 1902, 81, 495).

The rapid formation of the diacetyl derivative cannot, as has been suggested, be regarded as due to the direct action of the anhydride on the aniline, thus:



for the monoacetyl derivative is just as easily converted into the diacetyl compound as the aniline; moreover, in the treatment of the aniline with the anhydride, the monoacetyl derivative can always be recognised in the early stages of the acetylation. Sudborough's view that the readiness of diacetylation is conditioned by the stability of an acetate formed from the monoacetyl derivative and the acetic anhydride is not open to the same objection.

When the di-*o*-substituted aniline has two or more methyl (or alkyl) groups as substituents in the nucleus (xylenes, *p*-cumene, &c.), one of

which group is in juxtaposition to the amino-group, acetylation is normal.

We have made the observation that the acetylation of such di-*o*-substituted anilines (for example, *s*-tribromoaniline) by acetic anhydride is enormously accelerated by strong acids. Hydrochloric, sulphuric, perchloric, and trichloroacetic acids have been used as catalysts. Nitric and chromic acids behave exceptionally, the former producing a nitroaminoaniline (Orton, Trans., 1902, 81, 490, 860), and the latter acting as an oxidising agent.*

The effect of the acid as an accelerator is made obvious by the following experiment. A solution of one gram of *s*-tribromoaniline in 20 c.c. of acetic anhydride was kept for a fortnight at the ordinary temperature. The solid was then precipitated by addition of warm water; it melted at 119° , the melting point of the pure aniline. A similar solution was treated with two drops of concentrated sulphuric acid (about 1 gram-molecular proportion), the mixture being kept at the ordinary temperature; at the end of ten minutes, it was poured into warm water; the solid which separated melted at 231° , the melting point of *s*-tribromoacetanilide being 232° (corr.).

The acetylation also takes place, but not so rapidly, if the proportion of acetic anhydride is reduced and the mixture diluted with glacial acetic acid.†

Experiment.—One gram of *s*-tribromoaniline was dissolved in a mixture of 40 c.c. of glacial acetic acid and 4.5 c.c. (15 gram-molecular proportions) of acetic anhydride to which 0.16 c.c. (1 gram-molecular proportion) of sulphuric acid (98 per cent.) was added. The mixture was maintained at the ordinary temperature. At the end of ten minutes, 91 per cent., and at the end of twenty minutes 98–99 per cent., of the aniline was found to be acetylated. The composition of the mixture was determined by estimation of the bromine.‡

* Since nitric acid and acetic anhydride convert the aniline into a nitroamine, $\text{ArNH}_2 + \text{HO}\cdot\text{NO}_2 = \text{ArNH}\cdot\text{NO}_2 + \text{H}_2\text{O}$, it might have been anticipated that anilides of sulphuric, for example, $\text{ArNH}\cdot\text{SO}_3\text{H}$, or of perchloric acid, $\text{ArNH}\cdot\text{ClO}_3$, could be produced. No indication of the presence of such substances was detected.

† The commercial acetic anhydride (puriss.) was found to contain traces of sulphate and chloride, which were removed by careful distillation. The acetic acid used by us was fractionated, and then melted at 16.1° . Hence it contained 0.3 per cent. of water.

‡ When in a mixture of *s*-tribromoaniline and *s*-tribromoacetanilide both substances are present in considerable proportion, separation is exceedingly difficult to bring about by recrystallisation from the usual solvents. It is possible, however, to extract the anilide from the mixture by addition of 10 per cent. of sodium hydroxide to a suspension of the solid in alcohol. The anilide entirely dissolves, and, if the liquid is sufficiently diluted with water, no aniline remains in solution in the dilute alcohol. If any diacetyl derivative, which is, of course, insoluble in the alkali, be present, it remains mixed with the aniline (compare Orton, Trans., 1902, 81, 495.)

Inasmuch as acetic anhydride is without action on *s*-tribromoaniline at the ordinary temperature and yet at the boiling point converts the aniline into the diacetyl derivative, trials have been made with acetic anhydride at temperatures varying between 70° and 100°, and with mixtures of acetic acid and anhydride at these temperatures and at their boiling point. In all cases, a slow acetylation took place.

Experiment.—(1) A solution of 1 gram of the aniline in 20 c.c. of the anhydride was heated at 75°; after two hours the product contained 25 to 30 per cent. of anilide. More prolonged heating showed that conversion of the mono- into the di-acetyl derivative followed hard on the formation of the former; the melting point of the product rose to a maximum at 192° in three hours, and then gradually fell until the melting point of the pure diacetyl derivative (125°) was reached (see p. 1246).

(2) A solution of 1 gram of the aniline in a mixture of 15 c.c. of acetic anhydride and 20 c.c. of acetic acid was boiled in a reflux apparatus. After six and a-half hours, some 50 per cent. of the aniline was converted into the monoacetyl derivative; after forty-eight hours, the transformation was complete; after ninety-six hours' boiling, no further change, namely, that of the mono- into the di-acetyl derivative, was detected.

Other anilines with like substituents, for example, 2:6-dibromo-4-nitro- and 2:4-dibromo-6-nitro-anilines, behave generally in the same way as 2:4:6-tribromoaniline. They are not only acetylated by acetic anhydride extremely slowly at 100°, but are converted in some cases with even greater readiness than the *s*-tribromoaniline into diacetyl derivatives when boiled with this reagent. In the presence of mineral acids, they form monoacetyl derivatives with great rapidity.

The result is very different when anilines of other constitution are treated in the manner described in the foregoing. The acetylation of an aniline in which only one ortho-position is occupied by a negative group is an extremely rapid process. When, for example, a solution of 0.5 gram of 2:4-dibromoaniline in 45 c.c. of glacial acetic acid to which 1.25 c.c. (6½ gram-molecular proportions) of acetic anhydride was added, was kept for five minutes at the ordinary temperature and then poured into boiling water, a quantitative yield of the corresponding anilide (m. p. 144°) was obtained. The addition of mineral acid depresses the speed of acetylation.

Thus, on addition of 2-gram-molecular proportions of hydrochloric acid to the mixture, the presence of the anilide in the product can only just be detected (by fractional precipitation of the solution by water) at the end of five minutes; in an hour, however, acetylation was complete.

A series of experiments on the acetylation of aniline demonstrate the inhibiting effect of acid on the speed of acetylation.

Aniline.	Glacial acetic acid.	Acetic anhydride.	Sulphuric acid.	Anilide.	Percentage of aniline acetylated.
A. 1 gram	20 c.c.	10 c.c. (9 gr.-mol.)	0	1.84 gr.	92
B. "	"	"	1 gr.-mol.	1.25 "	85.7
C. "	"	3.3 c.c. (3 gr.-mol.)	0	1.29 "	88.6
D. "	"	"	1 gr.-mol.	0.43 "	29.5

The four mixtures were kept for one and a-half hours at 10°, then poured into 50 c.c. of warm water, and the liquid, which was placed in a shallow glass dish, was evaporated at the ordinary temperature by drawing rapidly over it a current of air. The anilide, which separated in large crystals, was collected and weighed. In experiment A, the acetylation of the aniline, which was shown in other experiments to be complete in a few minutes, was probably quantitative, the solubility of the anilide in the dilute acetic acid accounting for the deficiency of 8 per cent. A comparison of A with B, and C with D, brings out very clearly the reduction of the rate of acetylation by the mineral acid.

Effect of the Nature of the Acid.—In testing the effect of acids other than sulphuric, difficulties arise, on the one hand, owing to the low solubility of the acid in the acetic acid or anhydride, and, on the other, in the preparation of the acids in a highly concentrated form. Nitric and chromic acids, which offer less difficulty in these respects, behave, as previously stated, exceptionally; the acceleration of acetylation is masked by other reactions, although traces of the acetyl derivative can be detected with each acid.

We have been able, however, to demonstrate satisfactorily the accelerating effect of hydrochloric, perchloric, and trichloroacetic acids.

A solution of 0.5 gram of *s*-tribromaniline in 10 c.c. of acetic anhydride to which was added 0.15 c.c. of a 37 per cent. solution of hydrochloric acid (1 gram-molecular proportion) was kept for one and a-half hours, and then poured into warm water. *s*-Tribromoacetanilide, which separated, melted at 227–229°, instead of at 232°. As hydrochloric acid is all but insoluble in acetic anhydride, the concentration of the acid, owing to its obvious escape from the solution, must have fallen below the initial value.

Experiments carried out in acetic acid solution, in which hydrochloric acid is somewhat more soluble, led to a similar result. The aniline and anhydride were in the molecular ratio of 1:15, 2 gram-molecules of the hydrochloric acid being present.

Perchloric acid was used in the form of a 5*N*-solution. In one

experiment, one gram of *s*-tribromaniline dissolved in 38 c.c. of acetic acid (98 per cent.) was treated with 5.45 c.c. (18.2 gram-molecular proportions) of acetic anhydride and 0.6 c.c. (1 gram-molecular proportion) of 5*N* (50.25 per cent.) perchloric acid. The mixture was kept for half an hour at the ordinary temperature and then poured into warm water. The solid material thus obtained, which was a mixture of *s*-tribromo-aniline and acetanilide, contained 10 per cent. of the latter.

Trichloroacetic acid accelerated the acetylation in a far less pronounced manner than the other acids which were tested. In an experiment similar to that just described, only 10 per cent. of the anilide was produced after twenty hours at the ordinary temperature.

Formation of Diacetylanilides.

The formation of diacetyl derivatives is aided by the presence of an acid, but in nothing like the same degree as that of the monoacetyl derivatives.

A solution of 0.2 gram of *s*-tribromaniline in 20 c.c. of acetic anhydride, to which 0.25 gram-molecular proportion of sulphuric acid was added, contained only the monoacetyl derivative after ten minutes. After remaining for three hours at the ordinary temperature, the formation of the diacetanilide was distinctly shown by the depression of the melting point from 231° (the melting point of the monoacetyl derivative) to 192–213°, but only after forty-eight hours was the diacetylation complete.

If, on the other hand, this mixture, containing the monoacetyl derivative and the sulphuric acid, was maintained at 70–80°, instead of at the ordinary temperature, a quantitative conversion into the diacetyl derivative was brought about in one hour. That the elevation of temperature alone is not the cause of this rapid production of the diacetyl derivative is shown by the fact that only after seven hours' heating of a solution of the monoacetanilide in acetic anhydride at 70–80° is some 70 per cent. of the diacetanilide formed.

At the ordinary temperature, no change was detected in a solution of the acetanilide in acetic anhydride after a long period. The mixture of acetic anhydride and acetic acid used by us (p. 1244), as the experiments described in the foregoing demonstrate, will not carry the acetylation further than the formation of the monoacetyl derivative.

The speed of diacetylation is markedly dependent on the constitution of the aniline. For example, when a nitro-group replaces the para-placed bromine atom, as in 2:6-dibromo-4-nitroaniline, monoacetylation in acetic anhydride solution is complete in five minutes in the presence of a quarter or even one-thirteenth gram-molecular pro-

portion of sulphuric acid. This is all the more remarkable, as the solubility of this aniline is such that on using 20 c.c. of anhydride for 1.5 gram of aniline, the major part of the base remains in suspension. If the aniline is somewhat finely divided, it dissolves very rapidly, the anilide partly separating. When the larger proportion of sulphuric acid is used, the formation of the diacetyl derivative follows quickly on that of the monoacetyl compound. In half an hour, the melting point of the solid product falls far below that of the acetanilide, and after two hours is that of the pure diacetyl derivative.

Acetylation of Phenols.

According to Skraup (*Mongleich.*, 1898, 19, 458), the acceleration of acetylation of hydroxy-groups by sulphuric acid appears to have been first observed and put into practice in the acetylation of cellulose, &c., by Franchimont (*Compt. rend.*, 1879, 89, 711). This chemist used the acid as an alternative to zinc chloride and similar reagents, and seemed to regard it as a dehydrating agent. This view, however, is untenable in the light of Skraup's results. The latter ascertained that mere traces of sulphuric acid had a very powerful effect on the acetylation of various hydroxy-compounds by acetic anhydride. Later, Freyas (*Bull. Soc. Ind. Mulhouse*, 1899, 44) tested the use of sulphuric acid in the acetylation of phenols, aldehydes, and amino-phenols, &c. Thiele's preparation (*Ber.*, 1898, 31, 1249) of acetyl derivatives of quinols by treatment of the corresponding quinones with acetic anhydride and sulphuric acid can scarcely be regarded as a reaction of the same type.

To test the effect of different acids, we have chosen *s*-tribromophenol, which yields an acetyl derivative (m. p. 82°), easily isolated and weighed. In the presence of 0.25 gram-molecular proportion of sulphuric acid, a solution of the phenol in a mixture of acetic acid and acetic anhydride (50 per cent.), kept at the ordinary temperature, contains only acetate after half an hour. On replacing the sulphuric acid by perchloric acid, acetylation is equally rapid. In the absence of acid, the phenol is unchanged after twenty-four hours. Nitric acid reacts with the phenol, bromine being eliminated, whilst hydrochloric and trichloroacetic acids scarcely produce an appreciable effect.

Part Played by the Acid.

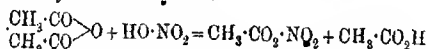
In our experiments, we have demonstrated that many acids, not only sulphuric acid, are accelerators of acetylation.* For this effect to

* In D.R.-P. 147033, a method of acetylating phenylglycine-*o*-carboxylic acid by saturating a solution in acetic anhydride with dry hydrogen chloride is described. The reaction appears to be ascribed to the formation of acetyl chloride.

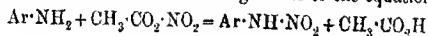
appear in the case of amines, our results show it to be essential that the amino-group should possess very little power of combining with acids to form ammonium salts. The speed of acetylation of the more basic anilines is lowered, not raised, by acids. When the amino-group is between two ortho-placed (negative) groups, its combining power with acids is, as is well known, greatly reduced, partly possibly on account of the negative character of these groups, and partly by virtue of a steric effect. Moreover, such an amino-group reacts very tardily with acetylating agents, such as acetic anhydride or acetyl chloride. Hence the specific accelerating action of the acid has an opportunity of making itself felt, and is no longer masked either by the conversion of the amino-group into the ammonium compound, which at the same time removes the acid, or by the too rapid action of the amino-group with the acetic anhydride.

It is not easy at present to state with precision what is the part played by the acid. Thiele and Winter (*Annalen*, 1900, **311**, 341) are of the opinion that in the acetylation of hydroxy-groups, an anhydride of sulphuric acid and acetic acid, $\text{CH}_3\cdot\text{CO}\cdot\text{O}\cdot\text{SO}_3\text{H}$, is first formed, which then reacts with the hydroxy-group. This substance was thought by Franchimont to be present in solutions of sulphuric acid in acetic anhydride, and to become converted into a sulphonie derivative of acetic acid, which he isolated.

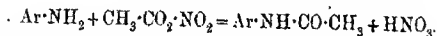
The peculiar behaviour of nitric acid may be accounted for in this way. The anhydride formed thus:



might react with the aniline according to one of the equations:



or



As a fact, the acetanilide forms a very small fraction of the product, whereas in the case of sulphuric acid the reaction is mainly, if not entirely, $\text{Ar}\cdot\text{NH}_2 + \text{CH}_3\cdot\text{CO}_2\cdot\text{SO}_3\text{H} = \text{Ar}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_3 + \text{H}_2\text{SO}_4$. The feeble effect of hydrochloric acid may also be due to a reluctance to form an anhydride, which is in this case acetyl chloride.

If the cause of the acceleration is to be found in a union of the acid and anhydride, it may be suggested that the complex is not a definite anhydride, but rather of the nature of an oxonium salt, $\begin{array}{c} \text{CH}_3\cdot\text{CO} \\ \diagup \quad \diagdown \\ \text{CH}_3\cdot\text{CO} \end{array} \text{O} < \begin{array}{c} \text{H} \\ \diagup \quad \diagdown \\ \text{X} \end{array}$.

On such a view less difference would be expected between the various acids than on the hypothesis that the formation of an anhydride is the first step.

The presence of an acid has another effect, which probably plays an important part when the acetylation is carried out in acetic acid

solution, that is, in greatly accelerating the interaction of water and the anhydride. In this way, the small quantities of water present in the acetic acid, or in the acid added as catalyst, are removed, and hence the reverse reaction, the hydrolysis of the anilide, is rendered impossible.

The effect of variation of the proportion of the acid on the rate of acetylation of amines and phenols, and a study of the dynamics of the reaction, are under investigation. The preliminary experiments indicate that the speed of acetylation is proportional to the square of the concentration of the acid, that is, doubling the concentration of the acid quadruples the velocity.

Preparation of the Monoacetyl Derivatives of Di-ortho-substituted Anilines.

Most anilines with two negative groups, such as the halogens and the nitro-group, in the ortho-position with respect to the amino-group can be quantitatively converted into their monoacetyl derivatives by the following procedure.

One gram of the aniline is dissolved in 40 c.c. of glacial acetic acid (98–100 per cent.), or in some cases when the aniline is very insoluble it is suspended in this quantity of solvent. Acetic anhydride is next added to the mixture; we have generally used 15 gram-molecular proportions of acetic anhydride to one gram-molecular proportion of aniline, that is, from about 4–6 c.c. of acetic anhydride for one gram of aniline, according to the molecular weight of the aniline. 0.08 c.c. (about four drops) of concentrated sulphuric acid is then introduced, and the mixture kept at the ordinary temperature for forty minutes to an hour. It is then poured into 100 c.c. of warm water, whereupon the anilide immediately separates. Increase of the acetic anhydride hastens the acetylation, but there is danger in some cases, if too large an excess of acetic anhydride is present, of the production of the diacetyl derivative.

We have found this method well adapted to the preparation of the monoacetyl derivatives of 2:4:6-tribromoaniline and other similar trihalogen anilines, for 2:6-dichloro- and 2:6-dibromo-4-nitroanilines, for 2:4-dichloro-6-nitroaniline, and for 3-bromo-5-nitro-*p*-toluidine.

2:6-Dibromoaniline appears to be somewhat exceptional, and is acetylated only if the proportion of anhydride is considerably higher than that given above. We have prepared the monoacetyl derivative by dissolving the aniline in acetic anhydride and adding the usual proportion of sulphuric acid. The acetylation was complete in two hours.

Preparation of Diacetyl Derivatives.

The di-*o*-substituted anilines just mentioned all form diacetyl derivatives with ease in the presence of mineral acid when the mixture of aniline and acetic anhydride is not diluted with acetic acid, but the rapidity of the reaction depends considerably on the constitution of the aniline. For example, 2:6-dibromo-*p*-nitroaniline yields a diacetyl derivative more readily than *s*-tribromoaniline.

s-*Tribromoacetanilide*.—This compound can be easily prepared in the following manner: 1 gram of *s*-tribromoaniline is dissolved in 40 c.c. of acetic anhydride to which 0.08 c.c. sulphuric acid ($\frac{1}{3}$ gram-molecular proportion) has been added. The mixture is placed on the water-bath (70–80°) for one hour, and then poured into 100 c.c. of warm water, whereupon the diacetyl derivative crystallises out in the pure state.

2:6-*Dichloro-4-nitroacetanilide*. — One gram of the aniline is suspended in 40 c.c. of acetic anhydride to which 0.08 c.c. of sulphuric acid has been added. The aniline passes into solution, the colour disappearing very rapidly. After remaining for two hours at the ordinary temperature, the mixture is poured into warm water. The diacetanilide separates directly in a nearly pure state, melting at 138° instead of 140°.

*The Acetylation of Heptabromo-*p*-hydroxydiphenylamine (s-Tribromophenyl-2':3':5':6'-tetrabromo-4-hydroxyphenylamine).*

In our investigation of the hydroxydiphenylamines (this vol., p. 314), we were unable to prepare the acetyl derivatives by heating the compounds with acetic anhydride and sodium acetate in the ordinary way. We find, however, that the monoacetyl derivatives, in which the acetyl group has replaced the hydrogen of the hydroxy-group, can be very easily obtained when a trace of sulphuric acid is added to the anhydride instead of the sodium acetate.

0.5 Gram of heptabromohydroxydiphenylamine is suspended in 50 c.c. of acetic anhydride to which 0.1 c.c. of sulphuric acid has been added. The mixture is warmed for fifteen minutes on the water-bath, when the compound completely dissolves. On cooling, the *acetate* separates in small, colourless, granular crystals, melting at 193°. The insolubility in warm alcoholic sodium hydroxide showed that the compound no longer contains a hydroxyl group:

0.1212 gave 0.2043 AgBr. Br = 71.74.

$C_{14}H_6O_2NBr_7$ requires Br = 71.78 per cent.

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CXX.—*The Hydrolysis of Amygdalin by Emulsin.*
Part I.

By S. J. MANSON AULD, Ph.D.

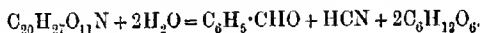
ENZYMES do not, as a general rule, occur singly, and it is frequently a matter of difficulty to isolate them from the mixture. The influence of these enzymes on one another has not yet been made the subject of much investigation, and it seems within the range of possibility that the presence of other enzymes may have a distinct effect on the action (compare Henry and Auld, *Proc. Roy. Soc.*, 1905, 76, B, 568). It is a matter of concern, therefore, that it has been just those ferments occurring with numerous others that have been employed for the study of enzymic action. Maltase, diastase, zymase, and lipase are all examples of this. It is also the case that many of these enzymes occur in numerous forms, and their source must of necessity be regarded as a factor both in their action and their examination. The maltase of yeast, of malt, and of germinating Indian corn (*Ber.*, 1895, 28, 1050) are very decidedly different in many respects, and a whole series of diastases is known.

For these reasons it seemed desirable to extend the investigation of enzymic action to emulsin, which, so far as we know, can be readily obtained in a state of "purity," that is, unmixed with other ferments. Further, only three distinct types of emulsin have been described, namely, the ordinary emulsin of sweet and bitter almonds, *Prunus amygdalus* var. *dulcis* and *Prunus amygdalus* var. *amara*, the emulsin of *Aspergillus niger*, to which Hérissé (Recherches sur l'Emulsin, *Thèse, Paris*, 1899) ascribes a special action, particularly in the rate of its decomposition of arbutin, and an emulsin associated with phaseolunatin (linamariu) in young flax plants and seeds and in *Phaseolus lunatus* beans. The latter enzyme was stated by Jorissen and Hairs (*Bull. Acad. roy. Belg.*, 1891, 21, 518) to decompose both amygdalin and linamarin, whilst the emulsin of sweet almonds was without action on the latter. It has been shown, however, that Jorissen and Hairs' emulsin is probably a mixture of ordinary emulsin with a maltase-like ferment, which causes the decomposition of phaseolunatin. It is possible, also, that Hérissé's *aspergillus* emulsin is identical with that of almonds, the evidence to the contrary being rather unsatisfactory.

A third fact renders the investigation of emulsin action necessary and advantageous; on Fischer's system of relating enzyme action to configuration, emulsin is the ferment which alone decomposes the β -glucosides, and in this way is complementary to maltase, which only attacks the α -isomerides.

The hydrolytic action of emulsin has not been the subject of much investigation. One or two old and practically valueless publications exist (compare Marckwort and Hüfner, *J. pr. Chem.*, 1875, [ii], 11, 202), and the only work of any importance on the subject is that of Tammann (*Zeitsch. physiol. Chem.*, 1892, 16, 271), who examined the action of emulsin at the same time as that of invertase and diastase. Although generally regarded as a valuable investigation, it contains, even in the small part devoted to emulsin, numerous inaccuracies, some of which will be referred to and discussed later. It must also be remembered that, at the time of the investigation, the law of mass was supposed to govern the course of enzyme action.

It was decided to study the action of emulsin principally with regard to its hydrolysis of amygdalin, the glucoside with which it is chiefly associated in the vegetable kingdom. Amygdalin and emulsin are co-existent, for example, in the seeds of *Prunus amygdalus*, and on macerating these with water the enzyme hydrolyses amygdalin with the production of one molecule each of benzaldehyde and hydrocyanic acid and two molecules of dextrose:



The "Emulsin" of Flax, and the Enzymes of Phaseolus lunatus and Manihot utilisima.

As previously mentioned, Jorissen and Hairs isolated a glucoside, linamarin, from germinating flax seeds, which they found to be unacted on by the emulsin of almonds. Co-existent with the glucoside, however, was found an enzyme which, besides hydrolysing linamarin, also decomposes amygdalin and salicin. Up to the present, the general view has been to attribute these different decompositions to the same ferment, and consequently to assume the existence of a special form of emulsin (see Oppenheimer, *Die Fermente*, p. 215). It has lately been shown that the cyanogenetic glucosides of flax, *Linum usitatissimum*, and of sweet and bitter cassava, *Manihot utilisima* and *Manihot dipii*, are identical with phaseolunatin obtained from *Phaseolus lunatus* beans (Dunstan, Henry, and Auld, *Proc. Roy. Soc.*, 1906, 78, B, 145, 152). It was first stated (Dunstan and Henry, *Proc. Roy. Soc.*, 1903, 72, 285) that phaseolunatin is hydrolysed by emulsin, but it has now been shown that this is not the case, although the enzyme accompanying phaseolunatin also decomposes the naturally-occurring β -glucosides (Dunstan, Henry, and Auld, *Proc. Roy. Soc.*, 1907, 79, B, 315). Similar observations were made with regard to the glucoside and enzyme of cassava. It has been further shown that in decomposing phaseolunatin, the enzymes associated with it in the various

plants act as maltase-like ferments, and in similarly decomposing amygdalin, &c., as emulsin-like ferments.

As it was thought that the ferments were probably mixtures, attempts were made to decide the question experimentally. It will be seen by a reference to tables III. and IV. that the hydrolysis of the β -glucosides proceeds much more slowly than that of phaseolunatin. The case is, in fact, almost exactly analogous to that of the maltase contained in extract of malt. It has been shown by Marino and Fiorentino (*Gazzetta*, 1906, 36, ii, 395) that this enzyme decomposes both α -glucosides, for example, maltase and α -methylglucoside, and β -glucosides, like amygdalin, salicin, &c. This dual action is ascribed to the same enzyme. It is probable that the maltase decomposition may be regarded as the primary action, and the emulsin-like hydrolysis as secondary. As the action of phaseolunata^{*}se might be explained in a similar manner, it was thought advisable to test it from this point of view.

Experiments were first made to determine whether a difference between the optimum temperatures of the actions on amygdalin and phaseolunatin could be observed, but very inconclusive results were obtained, and the attempt was eventually abandoned. The optima of both actions seemed to be between 40° and 50°.

It has been observed, in general, that the maltase ferments are more delicate than emulsin, and particularly more sensitive towards heat when in the dissolved state. Lintner and Kröber (*Ber.*, 1895, 28 1050) have shown, for example, that yeast maltase is destroyed at 56°, whereas emulsin retains a portion of its activity after being heated for some time at 70° (Henry and Auld, *loc. cit.*). It was thought possible, therefore, that if the action of phaseolunata^{*}se is due to two distinct enzymes, they might behave differently towards heat. This has actually been realised experimentally. By carefully heating the enzyme solution and observing the relative rates of decomposition of amygdalin and phaseolunatin, it has been possible to prove that the activity towards the latter glucoside is destroyed before that which causes the decomposition of the β -glucosides. This can readily be seen by reference to table V. In the present state of our knowledge of the enzymes, it is quite justifiable to conclude from these results that phaseolunata^{*}se contains two distinct enzymes, and these may be designated the α - and β enzymes, corresponding with their activity towards α - and β -glucosides. This is preferable to naming them maltase and emulsin respectively, for, although the former enzyme decomposes maltase and α -methylglucoside, the action in both cases is very slow and limited. The highest decompositions of α -methyl-

* The term "phaseolunata^{*}se" is used to represent the mixtures of enzymes in the three plant species without regard to their dual activity.

glucoside were obtained by employing a simple aqueous extract of white (cultivated) *Phaseolus lunatus* beans containing no cyanogenetic glucoside, obtained by macerating the meal with 12 volumes of water mixed with toluene. Fifty c.c. of this solution, added to 10 c.c. of a 3 per cent. solution of the glucoside, and kept at 40° for thirty hours, caused a decomposition of 9.3 per cent.

The Dynamics of the Hydrolysis of Amygdalin by Emulsin.

The dynamical study of an enzymic hydrolysis differs to a certain extent from that of an ordinary chemical reaction, principally because the products of change eventually exert a decided influence on the character of the hydrolyst. This action being very slight at the commencement of the hydrolysis of amygdalin by emulsin, the measurements of the velocity of reaction have been carried out, as far as possible, over short periods in the initial stages of the reaction.

Influence of the Concentration of Emulsin.—The effect of changing the concentration of emulsin on its action on amygdalin has been studied by Marckwort and Hüfner (*loc. cit.*), who added emulsin dissolved in glycerol to a solution of amygdalin and estimated the amount of glucoside decomposed after fifteen minutes. Their results are, however, practically worthless.

Tammann (*loc. cit.*) has also investigated the effect of increasing the quantity of emulsin in studying its action on salicin. Here, however, he followed the action by means of the polarimeter, and in consequence his results have no absolute value, owing to the fact that the rotatory power of a mixture of salicin and dextrose is not directly proportional to the amount of those substances present in solution. He finds, in accord with the previous workers, that the amount of salicin hydrolysed increases with the concentration of the enzyme, but apparently does not find any definite relationship between the emulsin present and the velocity of reaction.

By measuring only the initial velocities induced by varying quantities of emulsin in separate solutions, and thus avoiding any complications due to secondary action of the decomposition products, it has been found that with small concentrations of the onzyme the velocity of hydrolysis is proportional to the concentration of emulsin. As the concentration is increased this relationship ceases, and eventually a further increase in the quantity of emulsin present produces no corresponding increase in velocity. Taking the formula,

$$\frac{V_1}{V_2} = \left(\frac{C_1}{C_2}\right)^n,$$

where V_1 and V_2 are the velocities corresponding with

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the concentrations C_1 and C_2 , the following values of " n " may be calculated from the results given in table VI:

	V_1/V_2	n		V_1/V_2	n
1.	a/b 0.610	0.96	4.	d/e 0.731	1.23
2.	b/c 0.699	0.96	5.	e/f 0.791	1.32
3.	c/d 0.700	1.02	6.	f/g 0.696	1.36

In the above table, $n=1$ for moderate concentrations of enzyme, but increases considerably with increase of concentration. This agrees to a certain extent with the observations of E. F. Armstrong (*Proc. Roy. Soc.*, 1904, 73, 500) on the decomposition of lactose by kefir lactase. Sator (*Trans.*, 1906, 89, 131) obtained a constant value $n=1$ for alcoholic fermentation by live yeast, but Herzog (*Zeitsch. physiol. Chem.*, 1902, 37, 149) with "zymin" (yeast conserved with acetone) found $n=2$, and Euler (*ibid.*, 1905, 44, 53) with yeast juice obtained values for n varying from 1.29—1.67.

Influence of the Concentration of Amygdalin.—O'Sullivan and Tompson (*Trans.*, 1890, 57, 865) studied the course of the reaction of invertase on sucrose, and came to the conclusion that the course of enzymic hydrolysis follows the law of mass action, and that, like the corresponding inversion by acids, it may be expressed by the equation

for unimolecular reactions: $\log \frac{C_0}{C_t} = kt$. It was first definitely shown

by Adrian Brown (*Trans.*, 1902, 81, 373) that these conclusions cannot be supported. Working also with invertase, Brown found that the values of k calculated from the above equation gradually increased instead of remaining constant. About the same time, Victor Henri (*Compt. rend.*, 1901, 133, 891) formulated an empirical law to represent the course of inversion by enzymes, and arrived at

the conclusion that the expression $2kt = \log \frac{a+x}{a-x}$ was valid.

In the case of invertase, Adrian Brown and Horace Brown and Glendinning (*Trans.*, 1902, 81, 388) showed that, when the concentration of the hydrolyte is great compared with that of the enzyme, the decomposition is a linear function of the time, but changes to the logarithmic law in dilute solutions. This has been realised for other enzyme actions by different workers, particularly by E. F. Armstrong (*Proc. Roy. Soc.*, 1904, 73, 500, 516, 526; 74, 188, 195) for the sacroclastic enzymes.

It has now been shown that for emulsin, also, the velocity of reaction is independent of the concentration of amygdalin when the latter is present in large excess (table VII). Thus a constant quantity, and not a constant fraction, of amygdalin is hydrolysed in unit time. Larger quantities of amygdalin begin to produce a retarding effect on the action.

These results throw no light on the course of hydrolysis when the concentration of the amygdalin is allowed to change owing to the latter being consumed in the reaction, and when outside influences, such as the presence of the products of change, are brought into consideration. If, now, the experiments quoted in table VII are criteria of the velocity of hydrolysis throughout the reaction, the curve obtained by combination of time and hydrolytic activity should be a straight line. This, however, is not the case, for, although the velocity constants calculated from the equation $k = \frac{1}{t} \log \frac{a}{a-x}$

increase continually, the actual velocity decreases very considerably towards the end of the reaction, despite the fact that the hydrolysis does not approach completion. This may be seen from table VIII, which also, from the values of k , proves definitely that the hydrolysis does not follow the law of mass action. In the above expression, a represents the quantity of amygdalin originally present, and x the quantity decomposed after a time t . The non-constancy of the values of k cannot be due to an action in the reverse direction, for this would tend to decrease k , which actually increases during the course of action.

It was shown by Horace Brown and Glendinning (*loc. cit.*) for the diastatic fermentation of starch that the hydrolysis proceeded in two stages. In the first stage at the beginning of the reaction the decomposition was a linear function of the time, but later it actually followed the logarithmic law. The results obtained with emulsin may be interpreted in a similar manner. Up to a decomposition of nearly 50 per cent., equal amounts are hydrolysed in equal times. From this point onwards, D decreases steadily. The results were accordingly recalculated from the ninety minutes' decomposition, and the values of k found corresponding with this time as $t=0$ and the decomposition as $a=1$. Some of the numbers obtained are quoted in table X, and from the constancy of the values of k it would appear that the emulsin action also falls into two phases, a linear and a logarithmic, both more or less distinct from each other. The linear phase extends over a very considerable portion of the hydrolysis.

It is worthy of note that, although most of the enzymes have been shown to act apparently independently of the law of mass action, Fokin (*J. Russ. Phys. Chem. Soc.*, 1905, 38, 858) has quite recently asserted that the action of lipase, obtained, for example, from the seeds of *Chelidonium majus*, proceeds "like other catalytic actions, in accordance with Wilhelmy's logarithmic law." The mass of evidence being against such a view of enzymic action, it seems desirable that Fokin's results should be re-examined and the question of the procedure of lipoclastic action settled.

The fact that the latter part of the hydrolysis of amygdalin by emulsin proceeds according to the logarithmic law, might be explained by supposing that the shape of the curve of the action is merely fortuitous and due to partial destruction of the enzyme. Inhibition of the action by the products of change might also produce a certain constancy in the values of k . It has been proved for invertase by Adrian Brown, however, that where the concentration of enzyme is large compared with that of hydrolyte, the normal course of the hydrolysis obeys the law of mass action. The constancy of the recalculated k values might therefore be explained by assuming that the concentration of amygdalin had become sufficiently small to cause this second stage of the reaction. It was decided therefore to investigate the hydrolysis in dilute amygdalin solutions in the hope that this logarithmic stage would be actually realised.

The great difficulty in such experiments was to obtain a sufficient dilution without causing the reaction to proceed so quickly that it could not be followed quantitatively. Numerous experiments were carried out under varying conditions, and it was eventually found possible to trace the logarithmic phase of the hydrolysis (table X).

The generally accepted explanation of the fact that the velocity of enzyme hydrolysis is independent of the concentration of hydrolyte is the assumption that a compound is produced by interaction of enzyme and substance. If the compound thus formed lasts for an appreciable time, it will follow that, assuming the enzyme to be completely regenerated, alteration of the concentration of hydrolyte will have no effect, and equal amounts of the latter will be decomposed in equal times. Only when the concentration of the substance under examination becomes so small that a quantity of the enzyme remains uncombined will it have any effect on the course of hydrolysis. The results obtained with emulsin and amygdalin are completely in accord with this theory. It follows, for instance, that the quantity of enzyme, being completely combined with the hydrolyte, is a measure of the amount of compound formed, and therefore of the velocity of reaction. An increase in the quantity of enzyme should show a proportional increase in the rate of hydrolysis. This is, of course, actually the case, although other workers have obtained results not so easily explained. Herzog (*loc. cit.*), for instance, showed that the velocity of alcoholic fermentation is proportional to the square of the concentration of zymase. As pointed out by Sator (*loc. cit.*), however, the constancy of k in Herzog's results is probably due to partial decomposition of the enzyme. Fokin's results may possibly be explained in a similar manner, for lipase, as is well known, is a particularly sensitive enzyme.

Retardation of the Hydrolysis.—Enzyme action, in general, is capable

of inhibition by a large number of agents, and it has been in the study of the effect of retarding agents that any insight into their structure and action has been obtained.

Inhibition of enzyme hydrolysis may be caused in three ways: (a) By destruction of the enzyme; generally by coagulation through the action of substances of acid or basic character, sometimes by salts, and always by heat. (b) By combination of the enzyme with substances other than the hydrolyte. (c) By reverse action.

In the natural course of hydrolysis, only the last two come into consideration, and (c) only to a very small extent.

Retardation Caused by the Products of Reaction.—In the enzyme hydrolyses already studied, it has been shown that the products of reaction are the principal factors in causing the reaction to cease, and that by removal of these products the action will proceed to a finish (Tammann, *loc. cit.*).

The retardation caused by the products of the reaction of the hydrolysis of amygdalin by emulsin, namely, benzaldehyde, hydrocyanic acid, and dextrose, has been investigated by the addition of known quantities of these substances, both alone and together, to the reacting mixture and observing the change in the velocity of reaction. The results obtained are, on the whole, in agreement with some less comprehensive experiments carried out by Tammann in the same direction. Benzaldehyde and hydrocyanic acid have, it would appear, greater retarding effect on the action than dextrose, but here the results differ from those of Tammann, who attributed a stronger inhibiting action to hydrocyanic acid than to benzaldehyde. From tables XI, XII, and XIII this would not seem to be the case, and the values obtained are more in agreement with the views of Jacobson (*Zeitsch. physiol. Chem.*, 1892, 16, 367) and Marino and Fioretino (*Gazzetta*, 1906, 36, ii, 395), who contend that the action of emulsin is not affected by the presence of hydrocyanic acid. This, however, is also only partly correct, as hydrocyanic acid exerts a distinct retarding action.

It is impossible, of course, to draw any relationship between the retardation caused by benzaldehyde, hydrocyanic acid, and dextrose and the fact that they are products of reaction. The dextrose probably inhibits in this, as in other cases, by recombination with the enzyme to form complex carbohydrates, and the hydrocyanic acid will retard the action as a weak acid (see later). The behaviour of the benzaldehyde cannot be explained in the same manner. It seems, however, to be, in itself, a "poison" towards enzyme action. As is well known, phenol is generally without action on enzyme activity, and is frequently used for sterilising purposes. Salicylaldehyde, however, at once inhibits enzyme action, and has been used for this purpose in cases where it was

necessary to stop the hydrolysis at a certain point (E. F. Armstrong, Trans., 1903, 83, 1305). To the CHO group therefore must be ascribed "enzymicidic" properties, and benzaldehyde would naturally belong to this class. That this is actually the case may be seen from the following experiment carried out with invertase and sucrose. To two flasks containing 1.5 grams of sucrose dissolved in 15 c.c. of water were added 5 c.c. of a 1 per cent. solution of an invertase preparation, and in one of the flasks was placed three drops of benzaldehyde. After three-quarters of an hour at 31°, the respective amounts of sugar inverted as determined polarimetrically were found to be 51.0 and 39.6 per cent.

Inhibition of the Hydrolysis by Acids and Bases.—The action of acids on the activity of enzymes has been the subject of a considerable amount of investigation, but, unfortunately, the results obtained differ very considerably among themselves, even when obtained under apparently similar conditions. It is thus almost impossible to formulate a general law, and even for specific enzymes an agreement as to the effect of acids has been arrived at only in one or two cases. It can, of course, be said definitely that strong acids destroy enzyme activity, but we are here only concerned with low concentrations.

With regard to emulsin, the only experiments on record are those of Jacobson (*loc. cit.*), who investigated the property of various ferments of destroying hydrogen peroxide catalytically with evolution of oxygen. No quantitative experiments are on record, however, on the specific action of emulsin when influenced by dilute acids. Jacobson's results on the catalytic activity of emulsin are of interest in that they show that hydrochloric acid has no accelerating effect on the action even in dilute solutions.

In studying the "poisonous" effect of acids on the emulsin hydrolysis, dilute solutions of sulphuric, hydrochloric, acetic, and lactic acids were employed. The results obtained are given in tables XVI, XVII, XVIII, and XIX.*

The inhibiting effect of alkalis (potassium hydroxide and sodium hydrogen carbonate) has also been investigated, and the results are set forth in tables XX, XXI and XXII.

In its behaviour towards acids and alkalis, emulsin acts in a peculiar manner, distinct from the generally understood behaviour of most of the other unorganised ferments. In the first place, it would appear that the optimum action of emulsin does not lie in acid or alkaline solution, as is the case with the majority of enzymes. True, hydrocyanic acid in very small quantities has a slight accelerating effect on the action, but this increase in activity is not comparable, for example, with the effect of acid solutions on peptic proteolysis. Emulsin seems therefore to possess its optimum activity in neutral solution.

Of far greater importance is the fact elucidated that during their gradual inhibition of the power of emulsic hydrolysis, mineral acids and alkalis only partly destroy the activity, and that a neutralisation by alkalis or acids restores or reactivates the enzyme to a large extent. Senter (*loc. cit.*) has found that the inhibiting action of acids on hæmase is proportional to the concentration of the hydrogen ions, and from his results concludes that the enzyme is a weak base. Here, however, we have distinct primary evidence that emulsin is capable of combining with both acids and bases to form salts, from which it may be recovered in the usual way. The enzyme would thus appear to be at the same time both acid and base, and is in fact amphoteric in character. That neither of the functions is very strong is obvious from the fact that salt formation only takes place to a limited extent with the weaker acids and bases.

The possibility of enzymic salt formation at once raises the question of the nature of enzymes, and especially whether the ferments themselves are material substances, and capable of actual salt formation. Unless this is the case, one must assume that the energy centres of which the enzyme is composed are bound up so intimately with their material substrata that chemical reactions involving the latter produce absolutely corresponding effects on the former. In either case it must be concluded from these experiments that the activity of enzymes is more intimately bound up with the molecule of the protein compounds with which they are invariably associated, than has hitherto been generally supposed. The protein molecule itself is both acid and basic in character, and the addition of small quantities of acids and alkalis consequently causes protein salt formation. If, however, the acid or alkali is present in somewhat higher concentration, the structure of the protein is completely altered and acid-albumins and alkali-albuminates are produced. From these compounds, the protein cannot be regenerated. The connexion with enzyme activity seems obvious: we have, first of all with strong acids and alkalis of low concentrations, salt formation in the protein molecule, and a corresponding paralysis of the enzyme. Higher concentrations of hydrogen and hydroxyl ions produce the acid-albumins and alkali-albuminates, and destroy the enzyme activity.

Considering the dependence of the activity of emulsin on the presence of basic and acidic groups, and the fact that the glucosides hydrolysed contain no corresponding groups for attachment, that is, that the compound of enzyme and hydrolyte is probably not of the nature of a salt, it is probable that the catalytic activity is bound up with a combination involving a dynamic change in the enzyme molecule, such as would be expressed, for example, in a cyclic transformation of amino-acid into acid amide. Such a view of the

hydrolysis must, however, be reconciled with the fact that emulsin is essentially specific in its action and only decomposes glucosides which contain the β -lactonic grouping in the sugar residue. It is well known, however, that the protein molecule also contains carbohydrate groupings (compare Blumenthal and Mayer, *Ber.*, 1899, 32, 274), and it is not difficult to imagine combination of enzyme and hydrolyte only taking place when both contain the same or complementary similarly constructed sugar molecules. Such a view would be a literal fulfilment of Fischer's "lock and key" aspect of enzyme hydrolysis.

Extent of the Hydrolysis.—The hydrolysis of amygdalin by emulsin is not complete. This fact was first recognised by Liebig, who believed that the reaction proceeded only so long as the benzaldehyde produced dissolved in the water. This, of course, is not the case. Tammann (*loc. cit.*) also showed that the action is not finished, but his results differ from one another very considerably. Thus, although, in other parts of the paper, decompositions of amygdalin as high as 80 per cent. are implied, in the set of experiments devoted to the effect of increasing the quantity of emulsin at 40° a maximum decomposition of only 60 per cent. is obtained.

Quite recently, and after this research was well advanced, Caldwell and Courtauld (*Trans.*, 1907, 91, 670) repeated Tammann's experiments, and calculated the amount of change by observation of the rotatory power and by estimation of the benzaldehyde produced. They found that the maximum hydrolysis after sixty-seven and ninety hours amounted to 98.2 and 98.5 per cent. respectively. From estimations of the hydrocyanic acid produced, however, only 86.1 per cent. of the amygdalin appeared to be decomposed. Indeed, lower figures were invariably obtained from the hydrocyanic acid than from the benzaldehyde or rotatory power. No explanation of this deficiency is given, although such a deficiency is apparently to be ascribed to the hydrolysis of all cyanogenetic glucosides.

Employing the method described later for the estimation of hydrocyanic acid, no difficulty was experienced in obtaining much more profound decompositions of amygdalin calculated from a hydrocyanic acid basis than those described either by Tammann or Caldwell and Courtauld. Referring to table VIII, it will be seen that a decomposition of 93.3 per cent. is recorded in only twenty-two hours. In other cases, where the decomposition was measured over twenty-four hours and larger quantities of emulsin used, 97.0 per cent. of the amygdalin was found to be hydrolysed, but this was the maximum decomposition observed. It is suggested that Caldwell and Courtauld's results are somewhat high, as by carefully removing the hydrocyanic acid from alkaline solution with ferrous and ferric hydroxides and then esti-

inating the benzaldehyde by Ripper's method (*Zeitsch. anal. Chem.*, 1902, 41, 61), values have been obtained agreeing approximately with those from the hydrocyanic acid estimation. In some cases, indeed, they were slightly lower. The results obtained are given in table XXIII.

The Equilibrium, Reversibility.—Although the amount of glucoside remaining undecomposed (say 2 per cent.) falls far short of that claimed by Tammann, it is still sufficient to cause an assumption of equilibrium, an equilibrium which that author claims to be dependent on temperature.

Tammann himself tested the synthetic action of emulsin by placing glucose, hydrocyanic acid, and benzaldehyde on his tongue together with some emulsin, and awaiting the bitter taste of amygdalin. He failed to obtain any indication of reversible action by this means, however, which is scarcely surprising. No further experiments in this direction are on record, although Emmerling (*Ber.*, 1901, 34, 3810) has succeeded in synthesising amygdalin from mandelonitrile glucoside by the aid of maltase. An extensive series of experiments was therefore set on foot to test the synthetic action of emulsin as an explanation of incompleteness of the hydrolysis of amygdalin. The experiments were of two classes, namely, those where the amount of reacting substances present was measured from time to time, and that where an attempt was made after a considerable period to isolate amygdalin. Both series were wholly unsuccessful, and no account of the experiments need be given here.

Effect of Temperature on the Hydrolysis.—Temperature has a very marked effect on the velocity of all fermentation processes. The velocity of reaction is generally very small at low temperatures, and gradually increases to a point known as the *optimum* temperature of the ferment, from which point onward it again decreases until the ferment is completely destroyed by the heat action.

Tammann states that the temperature has a great effect on the amount of amygdalin decomposed by emulsin, that is, on the end point of the action, and uses this as a main argument against the incompleteness of the process being a chemical equilibrium. His views will apparently not bear investigation, however, as will be seen by contrasting his results with those quoted in table XXIII. The highest decompositions during the hydrolysis of salicin and amygdalin by emulsin were obtained between 45° and 50°, and, as previously mentioned, amounted only to about 80 per cent. At 40°, the end point is stated to be at a 60 per cent. hydrolysis of the amygdalin present. Contrast this, however, with the 93 per cent. and 97 per cent. hydrolyses obtained at the same temperature without any great difficulty, and the erroneous nature of Tammann's statement becomes apparent.

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Temperature Coefficients.—The general method of expressing the change in velocity of reaction due to change of temperature is to calculate the ratio of velocities for an interval of 10° . For most reactions, $\frac{k_{t+10}}{k_t}$ lies between 2 and 3.

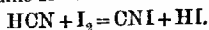
For the hydrolysis of amygdalin by emulsin, measurements were made at every 5° from 15° to 60° , and only initial velocities were taken, that is, while the velocity was still a linear time function. The observations were thus absolutely comparable. It will be observed from tables XXIV and XXV that the temperature-coefficient varies with the temperature, and only twice reaches the general value of between 2 and 3. The results are of the same order as those calculated from Tammann's figures for salicin.

Opportunity is taken here for correcting a serious error in this connexion in van't Hoff's "Lectures on Theoretical and Physical Chemistry, Part I." On pages 225 to 235 the velocity of the fermentation of salicin by emulsin is continually referred to as having a temperature-coefficient of 7.14 at from 60° — 75° . These figures are obtained by calculation from experiments by Tammann (*Zeitsch. physikal. Chem.*, 1895, 18, 433). This is so obviously erroneous, it having been shown that the velocity of reaction of emulsin hydrolysis is practically nothing at 70° (Henry and Auld, *loc. cit.*), that it is hardly necessary to turn to the original to find that the results refer to the rate of destruction of emulsin activity on heating. This, as is well known, increases with great rapidity with rise of temperature and thus affords a temperature-coefficient of abnormal size.

EXPERIMENTAL.

Analytical.—Three chief methods are open for the measurement of the hydrolysis, namely, estimation of the amount of hydrocyanic acid produced, measurement of the amount of dextrose formed, or observation of the change of rotatory power of the liquid. The two last methods are open to serious objection. Estimations of dextrose depending on its power of reducing alkaline copper solutions are difficult to carry out rapidly and accurately, and the fact that the character of the dextrose residues in amygdalin was unknown, made it impossible to follow the reaction by means of the polarimeter. To these objections must be added the possibility of the intermediate formation of a diglucose of unknown reducing and optical rotatory power. Determination of the amount of benzaldehyde formed or of the decrease in the quantity of amygdalin present offering no satisfactory solution of the question, it was decided to follow the hydrolysis by estimating the hydrocyanic acid produced. At first, this was estimated by means of standard

silver nitrate solution, but as this process could not be carried out with accuracy in the experimental liquid and consequently necessitated a distillation for each estimation, it was abandoned in favour of the modification of Fordos and Gelis' method (*J. pr. Chem.*, 1852, 59, 255) described by Dunstan and Henry (*Proc. Roy. Soc.*, 1903, 72, 287). This method consists in titrating the liquid containing hydrocyanic acid with a standard iodine solution:



Excess of sodium hydrogen carbonate solution is added to prevent an accumulation of hydroiodic acid.

As it was necessary to work at temperatures where a considerable

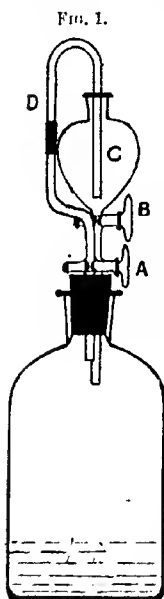


FIG. 1.

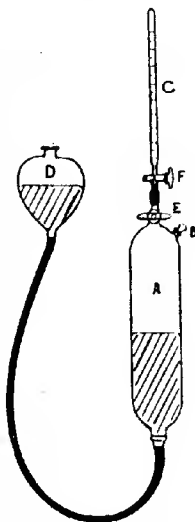
amount of the hydrocyanic acid formed would be in the gaseous state and would otherwise occasion a loss on opening the experimental vessels, special apparatus was devised to prevent any escape of vapour. In most of the experiments a separate vessel was used for each concentration of the reacting substances, and in such cases the small apparatus shown in Fig. 1 was employed. During the course of the reaction, the two taps, A and B, are kept closed. At the moment the hydrolysis is to be stopped, both taps are opened, and saturated sodium hydrogen carbonate solution flows into the bottle from the funnel C. At the same time, any escaping vapour is forced out through the side-tube D, and bubbles through the solution in the funnel by which it is carried back into the flask. When most of the bicarbonate solution has been run in, the taps are again closed, the contents shaken, and cooled under the tap. If the tap A alone is now opened, the remaining sodium hydrogen carbonate solution is sucked back through the side-tube, and frees it from any hydrogen cyanide remaining. The contents of the flask are then titrated

in the ordinary manner, using starch solution as indicator.

In those cases in which it was necessary to carry out a series of experiments in the same solution, and abstract aliquot parts for examination at stated intervals, a different arrangement was required, owing to the necessity of keeping all the hydrocyanic acid in the dissolved state. It was found by experiment that a surface of metallic mercury had no inhibiting effect on the action of emulsin on amygdalin, and the arrangement seen in Fig. 2 was consequently employed. The experimental vessel consists of the tube A, closed at the top by a tap,

and fitted with a stoppered side-tube, *B*, to facilitate the introduction of the enzyme and hydrolyte. The lower part of the tube is filled with mercury, which can be raised to the desired level by means of the reservoir *D*. The apparatus containing the amygdalin solution having acquired the necessary temperature by immersion in a thermostat, the emulsin is added, and the solutions well mixed. The tap *E* having been opened, *D* is now raised until the liquid just fills the vessel. The tap is now closed, and the whole apparatus immersed in the bath. To remove a stated volume of the liquid for examination, the bulb *D* is raised, and on opening the tap *E* the liquid is forced out into the tapered pipette *C*, which is connected with the tube *A* by a small piece of indiarubber tubing. The liquid is then run out into excess of sodium hydrogen carbonate solution, and the pipette washed out with the same liquid.

FIG. 2.



The sodium hydrogen carbonate thus effects a three-fold purpose. It absorbs the hydrocyanic acid, it is necessary for the iodine titration, and its addition at once stops the action of the emulsin. The accuracy of the last statement is seen at once from the following table:

TABLE I.

For each experiment, 25 c.c. of amygdalin solution (2 per cent.) were mixed with 2 c.c. of emulsin solution (2 per cent.). After twenty minutes, the sodium hydrogen carbonate (normal solution) was added, and the reaction allowed to proceed for another twenty minutes.

Time of action, mins.	NaHCO_3 added, c.c.	HCN formed, gram.	Amygdalin decomposed, per cent.
—	—	0.00130	12.7
20	0.25	0.00197	15.1
20	0.5	0.00141	13.4
20	1.0	0.00135	12.8
20	2.0	0.00130	12.7

$$T = 38.5^\circ.$$

For the hydrocyanic acid titration, it was found that *N*/50 iodine solution gave the best results, but *N*/100 iodine was also used in some cases where only a small decomposition had taken place. When *N*/10 iodine was employed, the results were not constant, but increased considerably on standing. This was probably due to the production of

Larger quantities of hydrogen iodide than could be absorbed at once by the sodium hydrogen carbonate, and the reaction being reversible, hydrocyanic acid would be regenerated.

Neither amygdalin nor its other decomposition products absorbs iodine, and the enzyme solution does so only after some time. As the complete estimation was usually carried out in one or two minutes, this involved no source of error, and the titration could be carried out in the experimental liquid.

The amygdalin employed was Merck's pure product recrystallised. The emulsin was also obtained from Merck's preparation, and was purified by dissolving in water and reprecipitating the filtered solution with 90 per cent. alcohol. The product obtained in this way dissolved completely in water. All solutions were kept sterile, generally by the addition of a little chloroform.

Phaseolunatae.

As the enzymes of *Phaseolus lunatus*, flax, and cassava all act in the same manner, it generally sufficed to carry out the experiments with one of them only. In most cases the enzyme obtained from Java beans was employed, and all the following experiments were carried out with it.

For the preparation of the enzyme, the beans, roots, or germinating seeds are dried thoroughly in the air, ground to a fine meal, and soaked with three volumes of water mixed with 1 per cent. of toluene, which is added for sterilising purposes. After several hours, the liquid is filtered, and allowed to stand in a vacuum desiccator over sticks of potassium hydroxide until all the hydrocyanic acid has been absorbed. The concentrated liquid is then poured into excess of alcohol, the precipitated enzyme quickly filtered and washed with a little alcohol, after which it is dried in a vacuum and finely powdered. If the substance is not completely redissolved by water, the process of solution and precipitation is again repeated.

The enzymes form fine white powders, capable of being kept in the active state for many months.

TABLE II.

Hydrolysis of Amygdalin by Phaseolunatae.

For each experiment, 10 c.c. of amygdalin solution (1 per cent.) were mixed with 30 c.c. of enzyme solution (2 per cent.):

Time of action, mins.	HCN formed, gram.	Amygdalin decomposed, per cent.
60	0.00294	84.5
120	0.00252	42.7
180	0.00301	50.9
240	0.00310	57.5

T = 40° C.

TABLE III.

Hydrolysis of Salicin by Phaseolunatae.

For each experiment, 10 c.c. of salicin solution (2 per cent.) were mixed with 30 c.c. of enzyme solution.

Time of action, mins.	Cu ₂ O formed, gram.	Glucose produced, gram.	Salicin decomposed, per cent.
—	0.0535	—	—
30	0.0924	0.0189	15.8
60	0.1313	0.0389	30.9
120	0.2019	0.0742	59.0
180	0.2265	0.0835	68.7

$T = 39.5^{\circ}$.

TABLE IV.

Hydrolysis of Phaseolunatin by Phaseolunatae.

For each experiment, 15 c.c. of phaseolunatin solution (2 per cent.) were employed.

Time of action, mins.	Weight of enzyme, gram.	HCN formed, gram.	Phaseolunatin decomposed, per cent.
30	0.2	0.0106	31.8
60	0.2	0.0206	61.8
90	0.1	0.0055	16.5
60	0.1	0.0104	31.2

$T = 40.0^{\circ}$.

TABLE V.

Action of Phaseolunatae on Amygdalin and Phaseolunatin after heating between 40° and 65°.

For the decomposition of the amygdalin, 20 c.c. of the glucoside were mixed with 10 c.c. of enzyme solution. For the phaseolunatin, 20 c.c. of glucoside (2 per cent.) were mixed with 5 c.c. of enzyme solution.

Temperature to which enzyme solution was heated.	Decomposition of amygdalin.				Decomposition of phaseolunatin.			
	Time of heating, mins.	Time of action, mins.	HCN formed, gram.	Amygdalin decomposed, per cent.	Time of action, mins.	HCN formed, gram.	Phaseolunatin decomposed, per cent.	
40	—	60	0.00136	5.8	80	0.00733	16.5	
		120	0.00262	11.1	60	0.01413	31.8	
45	60	60	0.00128	5.6	30	0.00591	13.3	
		120	0.00260	11.0	60	—	—	
50	120	60	0.00128	5.6	30	0.00355	8.9	
		120	0.00262	11.1	—	—	—	
55	60	60	0.00120	5.1	30	0.00160	3.6	
60	60	60	0.00101	4.3	60	—	—	
		120	0.00189	5.0	120	0.00019	1.1	
65	60	60	0.00042	1.8	60	—	—	
					120	—	—	

120

TABLE VI.

Influence of the Concentration of Emulsin on the Velocity of Hydrolysis.

In the following experiments, 50 c.c. of amygdalin solution (2 per cent.) were mixed with a 2 per cent. solution of emulsin.

t = time of action in minutes; A = the percentage of amygdalin decomposed; D = difference in successive readings. The hydrocyanic acid formed is given in grams.

Temp. = 41°.

a. 2 c.c. emulsin.				
t .	HCN.	A .	D .	
10	0.00060	3.6	3.6	
20	0.00125	7.3	3.7	
30	0.00190	11.1	3.8	
Mean velocity = 3.7 per cent. per ten minutes.				
b. 3 c.c. emulsin.				
10	0.00101	6.0	6.0	
20	0.00202	12.0	6.0	
30	0.00303	18.1	6.1	
Mean velocity = 6.05 per cent. per ten minutes.				
c. 4 c.c. emulsin.				
10	0.00146	8.9	8.9	
20	0.00279	17.1	8.2	
Mean velocity = 8.7 per cent. per ten minutes.				
d. 6 c.c. emulsin.				
10	0.00215	12.5	12.5	
20	0.00380*	23.2	10.7	
Mean velocity = 12.5 per cent. per ten minutes.				
e. 12 c.c. emulsin.				
5	0.00145	3.6	8.6	
10	0.00288	17.1	8.5	
Mean velocity = 17.15 per cent. per ten minutes.				
f. 25 c.c. emulsin.				
10	0.00363	21.6	—	
Velocity = 21.6 per cent. per ten minutes.				
g. 50 c.c. emulsin.				
5	0.00215	12.8	12.8	
10	0.00106	24.1	11.3	
Velocity = 24.1 per cent. per ten minutes.				

* This reading showing a great falling off in velocity for the higher decomposition was rejected, and the decomposition for the first ten minutes alone taken.

TABLE VII.

Influence of the Concentration of Amygdalin on the Hydrolysis in Strong Solutions.

For each experiment; 1 c.c. of emulsin solution (2 per cent.) was used, and the decomposition measured over a definite period.

Temp. = 39.5°. Vol. = 50 c.c.

Time of action, mins.	Weight of amygdalin used, grams.	HCN formed, gram.	Amygdalin decomposed, per cent.	Weight of amygdalin decomposed, gram.
20	0.1	0.00274	46.4	0.046
20	0.2	0.00274	23.2	0.046
20	0.3	0.00260	14.7	0.044
20	0.4	0.00260	11.0	0.044
20	0.6	0.00253	7.2	0.043
25	0.8	0.00348	7.4	0.059
25	1.0	0.00348	5.9	0.059
25	1.25	0.00340	4.6	0.058
25	1.5	0.00332	3.7	0.056

TABLE VIII.

Hydrolysis of Amygdalin by Emulsin in One Solution.

Volume of amygdalin solution (2 per cent.) = 300 c.c.

Volume of emulsin solution (2 per cent.) = 15 c.c.

15 c.c. were examined every ten minutes until 150 minutes had elapsed, when 10 c.c. only were taken.

Temp. = 40.0°.

Time of action, mins.	HCN formed, gram.	Amygdalin decomposed, per cent.	Difference per 10 mins.	$0.4343K = 1/t \log a/a - x.$
10	0.00096	6.1	6.1	255×10^{-3}
20	0.00707	45.2	5.4	295×10^{-3}
30	0.00859	54.9	4.8	309×10^{-3}
150	0.00784	75.3	4.6	347×10^{-3}
150	0.00963	93.3	—	41×10^{-3}

TABLE IX.

Old times, mins.	New times, mins.	$0.4343K = 1/t \log a/a - x.$
110	20	485×10^{-3}
140	50	488×10^{-3}
160	70	491×10^{-3}

Mean of total values (100—180 mins.) = 181×10^{-3} .

TABLE X.

Hydrolysis of Amygdalin by Emulsin in Dilute Solution.

Volume of (2 per cent.) emulsin solution used = 3 c.c.

Total volume of solution = 20 c.c.

Time of action, mins.	Amygdalin used, gram.	HCN formed,* gram.	Amygdalin decomposed, per cent.	$0.4343K = 1/\log a/a - x$
10	0.05	0.00138	0.0253	0.0304
10	0.03	0.00085	0.0155	0.0815
10	0.02	0.00053	0.0097	0.0297

* Estimated by means of N/100 iodine.

TABLE XI.

Inhibition of the Hydrolysis by Means of Dextrose.

For each experiment, 20 c.c. of amygdalin solution (2 per cent) were mixed with 1 c.c. of emulsin (2 per cent.).

Temp. = 40.0°.

Time of action, mins.	Dextrose added, gram.	Dextrose in gram-mol.	HCN formed, gram.	Amygdalin decomposed, per cent.
30	—	—	0.00319	13.5
30	0.2	0.0011	0.00314	12.3
30	0.4	0.0022	0.00298	12.6
30	0.75	0.0042	0.00279	11.8
30	1.0	0.0055	0.00274	11.6

TABLE XII.

Inhibition of the Hydrolysis by Means of Benzaldehyde.

For these experiments, a saturated solution of benzaldehyde was added to 20 c.c. of amygdalin (2 per cent.), mixed with 2 c.c. of emulsin solution (2 per cent.).

Vol. = 50 c.c. Temp. = 40.5°

Time of action, mins.	Benzaldehyde added,* c.c.	Benzaldehyde in gram-mols.	HCN formed, gram.	Amygdalin decomposed, per cent.
30	—	—	0.00613	20.0
30	1	$10^{-4} \times 0.314$	0.00599	25.8
30	5	$10^{-4} \times 1.570$	0.00545	23.1
30	10	$10^{-4} \times 3.141$	0.00511	21.7
30	15	$10^{-4} \times 4.715$	0.00471	20.0

* Benzaldehyde dissolved in 300 vols. of water.

TABLES XIII AND XIV.

Inhibition of the Hydrolysis by Means of Hydrocyanic Acid.

The hydrocyanic acid solution employed was found, on exact determination, to contain 0.112 per cent. of HCN. It was added to 20 c.c. of amygdalin solution (2 per cent.) mixed with 2 c.c. of the enzyme solution (2 per cent.).

Vol. = 50 c.c. Temp. = 40.0°.

Time of action, mins.	HCN added, c.c.	HCN in gram-mol.	HCN formed, gram.	Amygdalin decomposed, per cent.
30	—	—	0.00587	24.9
30	1	$10^{-4} \times 0.42$	0.00612	25.9
30	2	$10^{-4} \times 1.24$	0.00592	25.1
30	5	$10^{-4} \times 2.07$	0.00574	24.3
30	10	$10^{-4} \times 4.20$	0.00552	23.4

It will be observed that small quantities of hydrocyanic acid have a distinct accelerating effect on the action, and the following series of experiments may be quoted in which this action is intensified:

Temp. = 39.5°.

Time of action, mins.	HCN added, c.c.	HCN formed, gram.	Amygdalin decomposed, per cent.
30	—	0.01358	57.5
30	1.0	0.01391	59.0
30	3.0	0.01298	56.7
30	5.0	0.01338	55.0

TABLE XV.

Inhibition of the Hydrolysis by Means of the Mixed Products of Reaction.

Forty c.c. of 2 per cent amygdalin solution were mixed with 5 c.c. of emulsin solution, and the mixture kept in the thermostat at 40° in a stoppered bottle for four hours. The vessel and its contents were then heated for half an hour at 100° to destroy the enzyme, and then cooled to the ordinary temperature: 86 per cent. of the amygdalin had been decomposed. The product thus obtained was used for the inhibition experiments. For each estimation, 20 c.c. of amygdalin solution (2 per cent.) were mixed with 2 c.c. of emulsin (2 per cent.).

Temp. = 40.0°.

Time of action, mins.	"Reaction products" added, c.c.	Reaction products in gram-mol.*	HCN formed, gram.	Amygdalin decomposed, per cent.
30	—	—	0.00645	27.2
30	2	$10^{-4} \times 0.770$	0.00605	25.6
30	5	$10^{-4} \times 1.675$	0.00562	23.8
30	10	$10^{-4} \times 3.850$	0.00491	20.8

* Calculated as amygdalin.

Inhibition of the Hydrolysis by Acids and Alkalis.

TABLE XVI.

N/50 Sulphuric Acid.

For each experiment, 15 c.c. of amygdalin solution (2 per cent.) were mixed with 3 c.c. of emulsin solution (1 per cent.).

Temp. = 40·0°. Vol. = 50 c.c.

No. of experiment.	Time of action, mins.	H ₂ SO ₄ added, c.c.	HCN formed, gram.	Amygdalin decomposed, per cent.
1	15	—	0·00255	15·5
2	15	1	0·00241	14·6
3	15	2	0·00248	15·1
4	15	3	0·00223	13·6
5	15	5	0·00047	2·8
6	15	10	0·00011	0·6
7	15	15	—	—
8	15	20	—	—

Nos. 7 and 8 were exactly neutralised with dilute sodium hydroxide, and the mixture allowed to remain for another fifteen minutes at the same temperature. At the end of that time, No. 7 showed a decomposition of 3·4 per cent. of the amygdalin. After standing for a longer period, the odour of bitter almonds became very strong, showing the presence of a considerable quantity of active emulsin. No. 8 required a longer time for the signs of decomposition to appear.

TABLE XVII.

N/20 Hydrochloric Acid.

Quantities as before.

Temp. = 40·0°.

No. of experiment.	Time of action, mins.	HCl added, c.c.	HCN formed, gram.	Amygdalin decomposed, per cent.
1	15	—	0·00257	15·5
2	15	1	0·00192	11·6
3	15	2	0·00045	2·7
4	15	3	0·00015	0·9
5	20	5	—	—
6	10	10	—	—

As in the previous case, the last two experiments of the series were completed by exactly neutralising the liquid with sodium hydroxide and allowing the action to proceed as before. It was again found that the emulsin had been re-activated, although only to a small extent. No. 5 showed a decomposition of about 4 per cent. after fifteen minutes at 40°, but the activity of the emulsin in No. 6 had been nearly destroyed, for only after many hours was a faint odour of bitter almonds detectable.

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TABLE XVIII.

N/20 Acetic Acid.

Quantities as before.

Temp. = 40.5°. (New 1 per cent. emulsin solution used.)

Time of action, mins.	Acetic acid added, c.c.	HCN formed, gram.	Amygdalin decomposed, per cent.
15	—	0.00291	17.7
15	1	0.00281	15.9
15	2	0.00250	15.2
15	3	0.00232	14.1
15	5	0.00207	12.6
15	10	0.00178	10.8
15	15	0.00135	8.2

TABLE XIX.

N/20 Lactic Acid.

Quantities as before.

Temp. 40.5°.

Time of action, mins.	Lactic acid added, c.c.	HCN formed, gram.	Amygdalin decomposed, per cent.
15	—	0.00293	17.8
15	1	0.00268	16.3
15	3	0.00214	13.3
15	5	0.00192	12.7
15	10	0.00144	8.7
15	15	0.00097	5.9
15	20	0.00056	4.0

Bouchardat (*Compt. rend.*, 1845, 20, 111) has stated that acetic acid has no effect on the hydrolysis of amygdalin by emulsin, but from the above tables it is obvious that this empirical statement is erroneous, and that both acetic and lactic acids have a distinct inhibiting effect.

TABLE XX.

N/50 Potassium Hydroxide.

For each experiment, 15 c.c. of amygdalin solution (2 per cent.) were mixed with 3 c.c. of emulsin (1 per cent.).

Vol. = 50 c.c. Temp. = 40.5°.

No. of experiment.	Time of action, mins.	KHO added, c.c.	HCN formed, gram.	Amygdalin decomposed per cent.
1	15	—	0.00293	17.8
2	15	1	0.00275	16.7
3	15	2	0.00194	11.7
4	15	3	0.00025	1.5
5	15	5	—	—
6	15	10	—	—

After fifteen minutes, No. 6 was exactly neutralised with dilute hydrochloric acid, and allowed to remain in the thermostat for a further twenty-five minutes. At the end of that time, very strong odour of benzaldehyde and hydrocyanic acid could be detected, and on examination it was found that nearly 8 per cent. of the amygdalin had been decomposed. To confirm this remarkable re-activating of the emulsin, further experiments on neutralisation of the alkali were carried out.

TABLE XXI.

Quantities as before.

Temp. = 40.5°.

No. of expt.	KHO added, c.c.	Time of action of KHO, mins.	Time of action after neutralisation, mins.	HCN formed after neutralisation, gram.	Amygdalin decomposed after neutralisation, per cent.
6*	10	15	25	0.00131	7.9
7	10	30	30	0.00084	5.6
8	15	15	30	0.00125	7.6
9	20	20	30	0.00104	6.2

* Table XX.

Similar results to the above were obtained with a saturated solution of sodium hydrogen carbonate, the re-activation being very marked. The experiments were carried out originally when studying the inhibiting action of sodium hydrogen carbonate with a view to its utility for stopping the emulsin action. In experiments Nos. 3, 4, and 5, in table I, half the experimental liquid was used for determination of the hydrocyanic acid, and the remainder neutralised with hydrochloric acid, and replaced in the thermostat.

TABLE XXII.

N-Sodium Hydrogen Carbonate.

No. of expt.	Time of action, mins.	HCN formed, gram.	Amygdalin decomposed, per cent.
3	20	0.0046	24.4
4	20	0.0041	21.7
5	20	0.0039	20.1

Extent of the Hydrolysis.

TABLE XXIII.

Temp. = 40.0°.

Time of action, hours.	Emulsin added (2 per cent.), c.c.	Amygdalin solution (2 per cent.), c.c.	Decomposition from HCN, per cent.	Decomposition from C_6H_5CHO , per cent.
20	10	75	93.4	94.0
24	15	75	97.0	96.5
16	3	15	91.7	91.0

Temperature Coefficients.

TABLE XXIV.

In the first columns are given the times of the reaction (t), in the second the amount of hydrocyanic acid formed, in grams, and in the third the amount of amygdalin decomposed, per cent.

$T=15^{\circ}$.			$T=40^{\circ}$.		
t .	HCN.	D .	t .	HCN.	D .
15	0.00077	4.68	15	0.00400	24.33
30	0.00180	9.40	30	0.00785	47.77
45	0.00230	14.00			
$T=20^{\circ}$.			$T=45^{\circ}$.		
t .	HCN.	D .	t .	HCN.	D .
15	0.00149	9.06	15	0.00470	28.46
30	0.00286	17.40	20	0.00890	53.07
45	0.00429	26.10			
$T=25^{\circ}$.			$T=50^{\circ}$.		
t .	HCN.	D .	t .	HCN.	D .
15	0.00177	10.77	10	0.00413	25.54
30	0.00354	21.60	15	0.00625	38.04
			30	0.01081	65.82
$T=30^{\circ}$.			$T=55^{\circ}$.		
t .	HCN.	D .	t .	HCN.	D .
15	0.00250	15.21	15	0.00486	29.58
30	0.00492	30.00			
$T=35^{\circ}$.			$T=60^{\circ}$.		
t .	HCN.	D .	t .	HCN.	D .
15	0.00356	21.66	10	0.00300	18.30
30	0.00679	41.30	15	0.00445	27.08

The values of K , calculated for each temperature from the fifteen minute decomposition values are given in the following table, together with the ten-degree ratios calculated from them.

TABLE XXV.

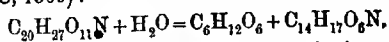
Temperature.	K .	k_{t+10}/k_t .	Tammann's value for salicin.
15°	0.01393	$k_{25}/k_{15} = 2.37$	
20	0.02635	$k_{30}/k_{20} = 1.81$	
25	0.03299	$k_{35}/k_{25} = 2.14$	2.52
30	0.04777	$k_{40}/k_{30} = 1.63$	1.52
35	0.07068	$k_{45}/k_{35} = 1.37$	
40	0.08071	$k_{50}/k_{40} = 1.71$	1.79
45	0.09696	$k_{55}/k_{45} = 1.04$	
50	0.13340		
55	0.10152		
60	0.09142		
72-73	nil*		

* Henry and Auld (*loc. cit.*).

CXXI.—*The Hydrolysis of Amygdalin by Emulsin.*
Part II.

By S. J. MANSON AULD, Ph.D.

By the action of an extract of yeast (Hefenenzym), amygdalin is hydrolysed with* the separation of only one molecule of glucose and the formation of a true glucoside, mandelonitrile glucoside (Fischer, *Ber.*, 1899, 28, 1509):



Mandelonitrile glucoside is hydrolysed by emulsin into benzaldehyde, hydrocyanic acid, and glucose.

From the above decomposition of amygdalin by yeast extract, the active enzyme of which was supposed to be maltase* (the ferment which decomposes maltose into two molecules of glucose), Fischer assumed that amygdalin is a derivative of maltose or of an exactly similarly constructed sugar. Latterly it has been generally the custom to regard amygdalin as the maltoside of benzaldehyd-cyanohydrin, and as such it is described in most books of reference. Thanks chiefly to the work of Emil Fischer, it is now practically certain that whilst emulsin only decomposes β -glucosides, maltase will only hydrolyse those glucosides which are derived from α -dextrose, hence there exists a distinct stereochemical relationship between these sugars and their specific enzymic hydrolysts.

These facts seemed to render it probable, or indeed certain, that the two molecules of glucose in the biose residue of amygdalin are not of similar constitution owing to their different behaviour towards the complementary enzymes, emulsin and maltase. It was first pointed out by the author (*Proc.*, 1907, 23, 72) that amygdalin is probably the derivative of an unknown $\alpha\beta$ -disaccharide capable of hydrolysis both by emulsin (β -enzyme) and maltase or amygdalase (α -enzyme). This view has since been confirmed by Rosenthaler (*Arch. Pharm.*, 1907, 245, 684). It was also pointed out that in the hydrolysis of amygdalin by emulsin the decomposition could take place in three ways, depending on the mode of attachment of the enzyme to the glucoside molecule. Either mandelonitrile glucoside and dextrose are first produced with subsequent hydrolysis of the former, or benzaldehyd-cyanohydrin and the disaccharide are formed and the latter

* It has now been shown by Caldwell and Courtauld (*Proc. Roy. Soc.*, 1907, 79, B, 350) that the yeast enzyme which hydrolyses amygdalin is not identical with maltase. This, however, has no effect on the above arguments as "amygdalase" is also an α -enzyme.

then resolves into two molecules of dextrose, or, lastly, amygdalin may undergo fission into the three components by direct abstraction of the dextrose residue attached to the benzaldehydecyanohydrin molecule.

Thanks to the admirable work of E. F. Armstrong on the correlation of the stereoisomeric α - and β -glucosides with the corresponding glucoses (Trans., 1903, 83, 1305), the first part of the problem could be attacked in the same manner as was adopted for the determination of the structure of the α -glucoside phaseolunatin (Dunstan, Henry, and Auld, *Proc. Roy. Soc.*, 1907, 79, B, 315). This method depends on the formation of sugar from the glucoside by hydrolysis and observation of its change of rotation on assuming the ordinary form of glucose which has been shown by Lowry (Trans., 1903, 83, 1314) to be an equilibrium mixture of two stereoisomerides. The production of equilibrium is hastened by the addition of a drop of alkali.

Rotation of Amygdalin.—With regard to the optical rotation of amygdalin, two different numbers are recorded. Bouchardat (*Compt. rend.*, 1844, 19, 1175) found for amygdalin, dried over lime at 45°, $[\alpha]_D -35.5^\circ$, and this value is still quoted in many books of reference. Schiff (*Ber.*, 1899, 32, 2701), repeating the experiments, obtained the value -40.26° , and declared Bouchardat's figures to refer to $[\alpha]_A$ and not to $[\alpha]_D$. Owing to these different results, the rotation of amygdalin was carefully measured, with the result that Schiff's rotations were also found to be not quite correct, the average rotation found being $[\alpha]_D -41.36'$. For 3.883 per cent. Schiff found $[\alpha]_D -41.1^\circ$.

Amygdalin, per cent.	<i>l.</i>	α_D^{20} .	$[\alpha]_D^{20}$.	(Schiff.) $[\alpha]_D^{20}$.	$[\alpha]_D$, calculated from Bouchardat's results by Schiff.
1.636	200	1°22'	41°16'	—	—
3.272	200	2 45	42 1	40°18'	41°57'
5.418	200	4 30	41 31	—	—
* Mean = 41°36'.					

Characterisation of the Dextrose Residues in Amygdalin.—Owing to the comparative slowness with which the yeast enzyme attacks amygdalin and the consequent spontaneous production of equilibrium in the dextrose which is formed together with the one molecule of mandelonitrile glucoside, it was found impossible to identify the sugar by the method proposed by E. F. Armstrong. To determine the nature of the second dextrose molecule, namely, that attached to the benzaldehydecyanohydrin nucleus, the decomposition of mandelonitrile glucoside by emulsin was employed. The mandelonitrile glucoside was prepared from amygdalin by the action of yeast extract according to the directions given by Fischer (*Ber.*, 1895, 28, 1509). After recrystallisation from chloroform it melted at 148,

and a proof of its purity was obtained by analysis. 0.5 Gram of emulsin was added to 5 grams of mandelonitrile glucoside dissolved in 50 c.c. of water, thoroughly mixed by shaking and kept in the thermostat in a stoppered bottle at 40°. For each observation, a few c.c. of the liquid were withdrawn, mixed with a small definite volume of alumina cream, and filtered through asbestos. The rotation of the clear liquid was then observed, before and after adding a drop of ammonia solution to establish equilibrium. Great care was taken to avoid the presence of any traces of alkali which might induce premature equilibrium, as in some cases it was found that the presence of a small proportion of tap-water was sufficient immediately to cause the dynamic change:

Time of action, hours.	Initial rotation.	Rotation after adding alkali.	Change of rotation.
—	-1°45'	-1°48'	0°0'
0.5	-1 18	-1 4	+0 14
1.0	-0 45	-0 20	+0 25
1.5	-0 22	+0 2	+0 24
24.0	+0 33	+0 35	+0 3

Taking into account the following rotations:

Mandelonitrile glucoside	-26.1°
α -Glucose.....	+105.0
β -Glucose	+22.0
Equilibrium mixture of α + β -glucose	+52.5

it is obvious from the results set forth above that in the decomposition of mandelonitrile glucoside there is primarily liberated the low rotating β -glucose, which, on the addition of ammonia, is at once transformed into the equilibrium mixture of higher rotation, thus proving, what has been generally assumed, that Fischer's glucoside is a β -glucoside. As a result of this, it is certain also that the dextrose residue of the amygdalin biose which is attached to the benzaldehydecyanohydrin nucleus has also a β -configuration.

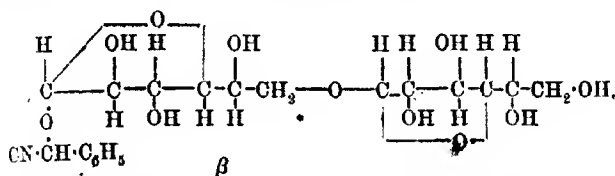
Although, as mentioned previously, it is impossible similarly to obtain direct evidence of the remaining dextrose molecule, the result can be attained by utilising the decomposition of amygdalin itself in a manner similar to that used for mandelonitrile glucoside. If both molecules of the biose are of β -configuration the positive change in rotation should be greatly increased, whereas, if the second molecule is derived from α -glucose, the optical rotation of the sugars produced on liberation with emulsin will to a certain extent neutralise each other, and on production of the equilibrium there will be no change, or only a very slight decrease in the rotation. This was actually found to be the case, as by using strong solutions of amygdalin a slight decrease in the rotation could be detected:

Temperature = 40.5°.

Weight of amygdalin in 50 c.c. of H ₂ O ₂ , grams.	Weight of emulsin added, gram.	Time of action, hours.	Initial rotation.	Rotation after adding alkali.	Change of rotation.
4.45	0.3	—	-6°48'	-6°48'	0° 0'
4.45	0.3	0.5	-3 54	-4 4	-0 10
4.45	0.3	1.0	-1 30	-1 45	-0 15
4.45	0.3	2.0	+2 51	+2 43	-0 8
4.45	0.3	24.0	+6 26	+6 26	-0 0
3.8	0.25	—	-4 48	-4 48	-0 0
3.8	0.25	0.66	-3 9	-3 18	-0 9
3.8	0.25	1.33	-0 23	-0 33	-0 10
3.8	0.25	20.0	+2 14	+2 14	0 0

Rotations measured in 2-dcm. tube.

From these results it would therefore seem to have been definitely proved that the biase from which amygdalin is derived is not maltose, but an $\alpha\beta$ -diglucose, and that amygdalin should be formulated as follows:



(Of extreme interest in this connexion is the fact, made apparent by the following experiments, that maltose, unlike glucose, has practically no inhibiting effect on the hydrolysis of amygdalin by emulsin,

Effect of Maltose on the Velocity of Hydrolysis.—For each experiment, 15 c.c. of 2 per cent. amygdalin solution were mixed with 3 c.c. of emulsin solution:

Temperature = 41.5°.

Time of action, mins.	Maltose added, gram.	HCN formed, gram.	Amygdalin decomposed, per cent.
30	—	0.00287	17.46
30	0.05	0.00284	17.27
30	0.10	0.00281	17.10
30	0.20	0.00283	17.23
30	0.30	0.00280	17.04

Mode of Procedure of the Hydrolysis.—Taking into account the three possible methods of decomposing amygdalin by emulsin, it will be observed that each involves the production of different quantities of the end products. If mandelonitrile glucoside is formed as an intermediate product of the reaction and is hydrolysed more slowly than amygdalin (which seems to be the case), then estimation of the

hydrocyanic acid and the benzaldehyde formed should give (relatively) lower results than those obtained from the dextrose. The same holds good in the equilibrium stage of the hydrolysis, as practically no enzyme action is complete and consequently a certain amount of the intermediate product may be expected to remain undecomposed. Similarly, should the emulsin after attaching itself to the β -glucoside molecule, as it apparently must do in its rôle of β -enzyme, cause the intermediate formation of the unknown $\alpha\beta$ -disaccharide, then the dextrose estimations should fall below those of the hydrocyanic acid and benzaldehyde; only in the event of the enzyme causing the disruption of the amygdalin molecule by simultaneous cleavage of the "biase" and "cyanohydrin" linkings would hydrocyanic acid, benzaldehyde, and dextrose be formed in quantities corresponding with the ordinary equation of amygdalin hydrolysis. It will be observed that the first method leads to the apparent anomaly of amygdalin being decomposed in the same manner by both yeast enzyme (Caldwell and Courtauld's amygdalase) and emulsin, which enzymes are of course really complementary to each other in their action. From one or two preliminary experiments carried out it was originally thought that the biase was formed as an intermediate product. This view, however, had to be considerably modified after careful and exhaustive series of experiments had been carried out. It was eventually found, in fact, that estimations of hydrocyanic acid and benzaldehyde constantly gave lower results than those of dextrose.

Care had to be taken to obtain the maximum hydrolysis in as short a time as possible so as to avoid any error due to partial decomposition of hydrocyanic acid on standing. A correction had also to be applied for the reducing power of the enzyme added, which was found to be considerable.

To avoid repetition and to save space, only a certain number of the results obtained will be quoted, and all these are included in the following table:

Time of action, hours.	Amygdalin used, grains.	Emulsin used, gram.	HCN formed, gram.	Cu ₂ O formed (corrected), grama.	Decomposition from HCN, per cent.	Decomposition from C ₆ H ₁₂ O ₆ , per cent.*	Decomposition from C ₆ H ₅ CHO, per cent.†
0.5	0.4	0.03	0.00556	0.6090	23.5	27.8	—
1.0	0.4	0.03	0.01000	1.0520	42.5	48.0	—
1.25	0.4	0.03	0.01187	1.2800	50.2	58.4	49.9
2.25	0.4	0.03	0.01772	1.8610	75.0	85.1	75.8
16.0	1.2	0.10	0.06501	—	91.7	—	91.9
20.0	1.5	0.20	0.07685	2.0800	93.4	94.9	91.0
4.0	0.3	0.06	0.01430	1.9900	87.0	90.8	—
1.75	0.3	0.06	0.01330	1.9300	81.5	88.1	—
0.25	0.3	0.04	0.00469	—	23.4	—	28.6
24.0	1.5	0.30	0.07969	2.1358	97.0	97.5	96.5

* Estimated gravimetrically.

† Estimated by Ripper's method.

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These results make it appear certain that the reaction proceeds (at any rate mostly) in two stages, and that the bi-ose linking in amygdalin is less resistant towards emulsin than that of the benzaldehydecyanohydrin. In this way mandelonitrile glucoside is formed preferentially and should appear among the reaction products. By stopping the reaction at a suitable stage, Fischer's glucoside can actually be separated. 0.5 Gram of emulsin was allowed to act on 20 grams of amygdalin and the reaction stopped when 75 per cent. of the amygdalin had been decomposed as calculated from the hydrocyanic acid liberated. The liquid was boiled to coagulate the protein matter, filtered and evaporated to dryness with animal charcoal, the charcoal being subsequently extracted with dry ethyl acetate. After repeating this process, the concentrated syrup was allowed to stand, when the mandelonitrile glucoside separated in small needles, melting, after recrystallisation, at 148°.

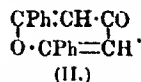
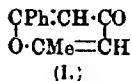
Considering this remarkable intermediate formation of mandelonitrile glucoside in the hydrolysis of amygdalin by emulsin, which is thus identical with that of acids (Caldwell and Courtauld, *Trans.*, 1907, 91, 666), it is curious that Fischer's glucoside has not so far been discovered co-existent with amygdalin in Nature.

CHEMICAL DEPARTMENT,
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CXXII.—*The Formation of 4-Pyrone Compounds from Acetylenic Acids. Part II.*

By SIEGFRIED RUHEMANN.

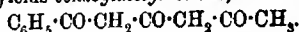
RECENTLY (*Trans.*, 1908, 98, 431) I have described a method of formation of 4-pyrone compounds, which is based on the reaction between ketones and ethyl phenylpropiolate in the presence of sodium ethoxide. Thus, two members of this group of substances have been obtained, namely, 2-phenyl-6-methyl-4-pyrone (I) and 2:6-diphenyl-4-pyrone (II):



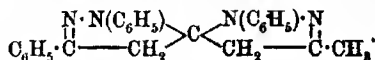
I have mentioned also (*loc. cit.*) that the formation of diphenylpyrone is accompanied by the production of a compound, $\text{C}_{12}\text{H}_8\text{O}_2$, which is characterised by the violet coloration of its solution in concentrated sulphuric acid. I have frequently studied the action of

sodium ethoxide on the mixture of acetone and ethyl phenylpropionate without having been able to trace a compound with similar properties; the product of the reaction consists of phenylmethylpyrone, the yield of which amounts to 48–50 per cent., of the unchanged acetylenic ester, and the corresponding acid.

The present paper deals with the study of phenylmethylpyrone, which I have carried out on lines similar to those adopted by F. Feist (*Annalen*, 1890, 257, 253) in his work on 2:6-dimethyl-4-pyrone. He showed that this compound, on treatment with baryta, is transformed into the yellow barium salt of diacetylacetone, which, with hydrochloric acid, yields the colourless triketone, $(\text{CH}_3\text{CO}\cdot\text{CH})_2\text{CO}$. He has not been able to accomplish the analogous change on using diphenylpyrone owing to the insolubility of this pyrone in water (compare *Ber.*, 1890, 23, 3726). I have repeated this experiment, but have also failed to isolate the triketone, dibenzoylacetone, from the product of the action of baryta on the pyrone. Phenylmethylpyrone, however, is readily transformed into a yellow barium salt, which, with hydrochloric acid, yields benzoylacetylacetone,

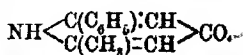


This compound resembles diacetylacetone in its behaviour. Feist has found (*loc. cit.*) that the latter triketone forms, with phenylhydrazine, a yellow diphenylhydrazone, which is produced, also, by the action of the hydrazine on 2:6-dimethyl-4-pyronecarboxylic acid; in this case, however, a colourless substance is formed at the same time which contains one molecule of water less than the dihydrazone. A compound, which in composition and properties resembles this substance, is produced on treatment of benzoylacetylacetone with phenylhydrazine. The fact that this compound is very stable and only slightly reduces Fehling's solution, even on boiling, points to the constitution:



This corresponds with the formula suggested by Feist for the colourless compound which is formed from dimethylpyronecarboxylic acid.

By the action of ammonia, benzoylacetylacetone is transformed into 2-phenyl-6-methyl-4-pyridone,



This substance has a characteristic behaviour which neither pyridone nor its dimethyl derivative seems to possess, namely, that its aqueous solutions readily gelatinise; this property renders its purification somewhat troublesome. I have prepared several salts of this base, but none of them exhibits this phenomenon. The ease with which β -diketones, for example, acetylacetone, react with aldehydes has

induced me to ascertain whether benzoylacetylacetone shows a similar behaviour; I have found, however, that in the presence of neither piperidine nor sodium hydroxide as catalytic agent does this triketone condense with benzaldehyde or salicylaldehyde.

EXPERIMENTAL.

Benzoylacetylacetone, $C_6H_5 \cdot CO \cdot CH_2 \cdot CO \cdot CH_2 \cdot CO \cdot CH_3$.

On adding a concentrated aqueous solution of baryta to phenyl-methylpyrone dissolved in boiling water, a yellow barium salt is precipitated which, when added to dilute hydrochloric acid, loses its colour and is transformed into benzoylacetylacetone. This substance is sparingly soluble in carbon disulphide, ether, or cold alcohol, but readily dissolves in boiling alcohol or chloroform; it crystallises from light petroleum, in which on boiling it is fairly soluble, in pale brown needles melting at $106-107^\circ$:

0.2213 gave 0.5716 CO_2 and 0.1182 H_2O . $C=70.44$; $H=5.93$.

$C_{12}H_{12}O_3$ requires $C=70.59$; $H=5.88$ per cent.

The triketone is readily dissolved by dilute potassium hydroxide, yielding a yellow solution; it is insoluble in cold, but soluble in hot sodium carbonate solution.

Action of Phenylhydrazine on Benzoylacetylacetone.

On adding water to the mixture of the triketone (1 gram), dissolved in alcohol, and phenylhydrazine (1.2 grams), an oily product is precipitated which, when stirred with alcohol, sets to a yellow solid. This is sparingly soluble in boiling alcohol, and, on cooling, crystallises in colourless prisms melting at $174-175^\circ$:

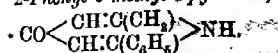
0.2015 gave 0.5800 CO_2 and 0.1100 H_2O . $C=78.50$; $H=6.06$.

0.2265 „ 30 c.c. N_2 (moist) at 17° and 756 mm. $N=15.28$.

$C_{22}H_{22}N_4$ requires $C=78.69$; $H=6.01$; $N=15.30$ per cent.

The formation of this substance is most probably proceeded by the production of the diphenylhydrazone of benzoylacetylacetone, which, however, at once condenses with loss of water. The fact that this compound is but slightly attacked by potassium hydroxide or hydrochloric acid, and only faintly reduces Fehling's solution on boiling, seems to support the formula given on p. 1282.

2-Phenyl-6-methyl-4-pyridone,



Benzoylacetylacetone is readily soluble in hot, concentrated ammonia; on evaporating the solution on the water-bath, a solid is left behind which is sparingly soluble in cold, but readily so in boiling water. The hot concentrated solution, after treatment with animal charcoal, deposits colourless, curved needles, and the mother liquor, after a short time, sets to a jelly which renders it impossible to collect the crystals. It is therefore necessary to filter them from the warm solution. The pyridone melts at 177—178°:

0.2100 gave 0.5970 CO_2 and 0.1155 H_2O . $\text{C} = 77.53$; $\text{H} = 6.11$.

0.2230 „ 14.8 c.c. N_2 (moist) at 18° and 755 mm. $\text{N} = 7.61$.

$\text{C}_{12}\text{H}_{11}\text{ON}$ requires $\text{C} = 77.84$. $\text{H} = 5.95$; $\text{N} = 7.57$ per cent.

The gelatinous product which separates from the mother liquor of the crystals seems to contain the same substance; this would follow from the fact that the solid which is left behind, on evaporation to dryness, gave the following analytical data:

0.2172 gave 0.6138 CO_2 and 0.1182 H_2O . $\text{C} = 77.07$; $\text{H} = 6.04$,

which do not appreciably differ from those required for phenyl-methylpyridone.

The pyridone dissolves in hot, concentrated hydrochloric acid, and the solution, on cooling, deposits colourless needles of the hydrochloride. This melts at 242°, after having begun to soften at 225°; it is not very soluble in cold, but readily so in boiling water:

0.2340 gave 0.1518 AgCl . $\text{Cl} = 16.05$.

$\text{C}_{12}\text{H}_{11}\text{ON} \cdot \text{HCl}$ requires $\text{Cl} = 16.03$ per cent.

On adding platinum tetrachloride to the aqueous solution of the hydrochloride, the *platinichloride* of the pyridone is precipitated in pale orange, microscopic needles:

0.3048 gave 9.6 c.c. N_2 (moist) at 19° and 764 mm. $\text{N} = 3.65$.

0.2068 left on ignition 0.0520 Pt . $\text{Pt} = 25.09$.

$(\text{C}_{12}\text{H}_{11}\text{ON})_2 \cdot \text{H}_2\text{PtCl}_6$ requires $\text{N} = 3.59$. $\text{Pt} = 24.94$ per cent.

The *picrate* is formed on mixing aqueous solutions of phenylmethylpyridone and picric acid. The emulsion which is first produced, soon sets to a crystalline solid, which is sparingly soluble in cold, but fairly readily in boiling water, and, on cooling, separates in yellow needles melting at 194—195°:

0.1986 gave 24 c.c. N_2 (moist) at 20° and 753 mm. $\text{N} = 13.59$.

$\text{C}_{12}\text{H}_{11}\text{ON} \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$ requires $\text{N} = 13.53$ per cent.

The *chromate* is precipitated in orange needles on adding chromic acid, dissolved in water, to the aqueous solution of the pyridone:

0.2368 gave 10 c.c. N_2 (moist) at 19° and 754 mm. $N = 4.81$.

$(C_{12}H_{11}ON)_2 \cdot H_2Cr_2O_7$ requires $N = 4.75$ per cent.

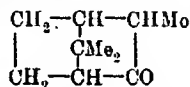
The salt does not melt, but, on heating, begins to blacken at about 155° ; it is sparingly soluble in cold, but readily so, in boiling water.

GONVILLE AND CAIUS COLLEGE,
CAMBRIDGE.

CXXIII.— α -Methylcamphor and Fenchone.

By WALTER HAXIS GLOVER.

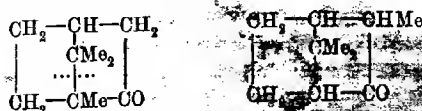
THE investigation described in this communication was undertaken primarily with the object of contrasting α -methylcamphor with fenchone, to which Wallach has assigned the formula



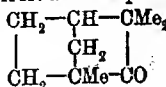
mainly because *m*-cymene is formed when it is heated with phosphoric oxide (*Annalen*, 1898, 300, 319). If fenchone possess the constitution represented by this formula, it should be similar to α -methylcamphor in its general chemical behaviour, as it is not to be supposed that the transference of a methyl radicle to the α -position would tend to alter the properties of the compound materially. As a matter of fact, the two substances are essentially different in chemical behaviour. They differ most markedly in their behaviour towards bromine. Minguin has stated (*Compt. rend.*, 1903, 136, 751)—and his observations have been confirmed—that α -methylcamphor yields on bromination a well-defined monobromo-derivative, namely, α' -bromo- α -methylcamphor; fenchone, when similarly treated, does not yield a bromo-derivative: in fact, bromofenchone is obtained as a somewhat ill-defined oil only when fenchone is heated with bromine in sealed tubes at 100° for twenty hours (Czerny, *Ber.*, 1900, 33, 2287). The two compounds also differ in that α -methylcamphor is as readily sulphonated by Reychler's method (*Bull. Soc. chim.*, 1898, [iii], 19, 129) as camphor itself, whilst fenchone resists sulphonation.

These two facts are alone sufficient to make it more than doubtful whether the constitution of fenchone be that suggested by Wallach.

The objection may also be raised to Wallach's formula that, since camphor yields *p*-cymene, fenchone should yield ortho-, not meta-, cymene:

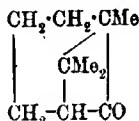


Semmler (*Chem. Zeit.*, 1905, 29, 1313), arguing from the fact that isocamphoronic acid, dimethylcarballylic acid and dimethylmalonic acid are products of oxidation of fenchone, has concluded that Wallach's formula is incorrect and has put forward the following:



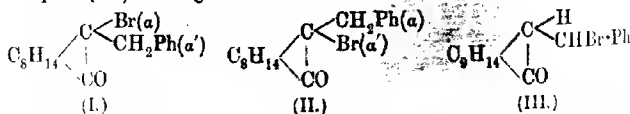
Although this formula foreshadows the difficulty with which fenchone is brominated, there is no obvious reason why such a compound should not yield a β -sulphonic acid with the same readiness as α -methylcamphor; moreover, the formula in no way gives expression to the production of *m*-cymene.

It is suggested that the following formula would better represent the formation of this hydrocarbon and would likewise show why fenchone should not be brominated readily nor be converted into a β -sulphonic acid by Reychler's method.



A monobromo-derivative of α -methylcamphor isomeric with that obtained directly from α -methylcamphor was prepared by Minguin (*loc. cit.*) by acting on methylenecamphor with a solution of hydrogen bromide in glacial acetic acid.

Haller and Minguin (*Compt. rend.*, 1900, 130, 1362; 1901, 133, 79) found that α -benzylcamphor on bromination gives rise to two stereoisomeric α' -bromo- α -benzylcamphors (I and II), which melt respectively at 94—95° and 90—91°; whilst the isomeride formed by adding hydrogen bromide to benzylidenecamphor is an α -bromo- α -benzylcamphor (III) melting at 146°.



Minguin therefore supposed, on the assumption that α -methylcamphor was the analogue of α -benzylcamphor, that the compound

obtained directly was α' -bromo- α -methylcamphor (IV) and that the isomeride was α -bromo- α -methylcamphor (V).



It seemed not improbable, however, that since these isomerides, like the isomeric α' -bromo- α -benzylcamphors, melt within a few degrees of each other, the melting points being 61° and 65° respectively, they might be stereoisomeric α -bromo- α -methylcamphors, thus:



Now Lowry has shown (Trans., 1906, 89, 1033) that α -mono-substituted derivatives of camphor, such as α -bromocamphor, are partly converted into their stereoisomeric forms by the addition of traces of sodium ethoxide to their alcoholic solutions, the change being accompanied by a change in the optical rotatory power of the solution. It therefore seemed possible that, by investigating the effect of alkali on the optical rotatory powers of alcoholic solutions of the two mono-bromo-derivatives of α -methylcamphor, the correctness, or otherwise, of the above supposition could be tested. However, neither of the alcoholic solutions of the isomerides showed any change in optical rotatory power on the addition of alkali, although, as was proved later, one of the isomerides is α -bromo- α -methylcamphor as stated by Minguin (*loc. cit.*). Further examination of α -methylcamphor and its β -substituted derivatives showed that these compounds, although, still containing an atom of hydrogen in the α -position, apparently do not undergo stereoisomeric change in alcoholic solution under the influence of alkali. It appears not improbable therefore that, under these conditions, only those α -mono-substituted derivatives of camphor undergo stereoisomeric change in which the substituting radicle is strongly negative in character, as was the case in the compounds investigated by Lowry, unless it be that, in the above cases, the change takes place very rapidly before the addition of alkali and escapes observation.

The action of potassium permanganate on the isomerides was first investigated. Although both are but slightly affected by this agent, nevertheless, under similar conditions, it is noticeable that the colour of the permanganate is discharged more readily and that more bromide is found in solution in the case of the compound described by Minguin as α -bromo- α -methylcamphor than in the case of α' -bromo- α -methylcamphor. Again, the former compound remains unaltered in the presence of cold nitric acid (sp. gr. 1.4), whereas the latter readily parts with its bromine

when similarly treated. This difference in the behaviour of the two compounds being scarcely that to be expected in the case of stereoisomerides, their comparative study was continued: finally it was found possible to brominate one isomeride, namely, the ω -bromo- α -methylcamphor, whilst the other isomeride, α -bromo- α -methylcamphor, remained unattacked.

The compound obtained by brominating α -bromo- α -methylcamphor is $\omega\alpha'$ -dibromo- α -methylcamphor, since it is identical with the compound obtained by the addition of bromine to methylenecamphor.

As regards the properties of the individual derivatives of α -methylcamphor described in this paper, little need be said. Generally speaking, they are very similar to the corresponding camphor compounds in their ordinary chemical and physical characteristics. As a rule, however, the melting point of the compound is lowered by the introduction of the methyl group into the α -position, whilst the specific rotatory power remains approximately the same; this will be seen by reference to the following table, in which are given the specific rotatory powers and melting points of the corresponding derivatives of d -camphor and α -methylcamphor.

Compound.	M. p.	$[\alpha]_D$.
Camphor	175°	+43° (alcohol)
α -Bromocamphor	76	+135 (alcohol)
Camphor- β -sulphonic acid.....	193	+21 (water)
Camphor- β -sulphonyl chloride	67–68	+31 (chloroform)
Camphor- β -sulphonamide	132	+1.5 (chloroform)
β -Bromocamphor	78	+19 (alcohol)
α -Methylcamphor.....	38	+30 (alcohol)
α' -Br.- α -methylcamphor	62.5	+180 (alcohol)
α -Methylcamphor- β -sulphonic acid.....	114–116	+18 (water)
α -Methylcamphor- β -sulphonyl chloride	33	+29 (benzene)
α -Methylcamphor- β -sulphonamide.....	150	–6.3 (chloroform)
β -Bromo- α -methylcamphor	55	+18 (alcohol)

Thus, although the introduction of the methyl group into the α -position involves the production of a third asymmetric carbon atom within the molecule, no marked change in the rotatory power is induced. This is what might be expected, since the greater the dissimilarity of the radicles occupying the $\alpha\alpha'$ -positions the greater is the change produced in the specific rotatory power of the compound. This is at once seen from the following examples:

Camphor	$[\alpha]_D$ +43°	α -Bromocamphor.....	$[\alpha]_D$ +135°
α -Methylcamphor	$[\alpha]_D$ +30	α -Chloro- α' -bromocamphor	$[\alpha]_D$ +19
α -Iodocamphor	$[\alpha]_D$ +160	$\alpha\alpha'$ -Dibromocamphor	$[\alpha]_D$ +40

A great difference exists, however, between the specific rotatory powers of the oximes of the two compounds. As was shown by Beckmann (*Annalen*, 1889, 250, 354), the oxime obtained from d -camphor has the specific rotatory power $[\alpha]_D$ –42°; that of the oxime prepared from α -methylcamphor is $[\alpha]_D$ +30° (both in alcoholic solu-

tion). It therefore seems not improbable that the two oximes have a different structure. In harmony with this conclusion is the fact that camphoroxime is soluble in alkali, whilst α -methylcamphoroxime is insoluble.

Reference may also be made here to the fact that α -methylcamphoroxime undergoes dehydration as readily as camphoroxime itself when heated with dilute sulphuric acid, showing that substitution in the α -position has no marked influence on the readiness with which the nitrile is formed.

In conclusion, mention may be made of what appears to be a case of isomorphism met with in the present investigation.

In an attempt to separate a mixture of camphor and its α -methyl homologue by bromination and subsequent fractional crystallisation of the resulting product, a substance was obtained which, although it melted within a degree of the temperature given by Minguin as the melting point of α' -bromo- α -methylcamphor, on analysis was found to contain more bromine than was required by theory. Subsequently, it was shown to be a mixture of $\alpha\alpha'$ -dibromo- and α' -bromo- α -methylcamphor, which remained practically constant in composition notwithstanding repeated crystallisation.

That the two compounds are in all probability isomorphous follows from the fact that they both crystallise in the orthorhombic system and have the axial ratios:

$\alpha\alpha'$ -Dibromocamphor	1.5778 : 1 : 2.0685 (Zepharovitch, <i>Monatsh.</i> , 1892, 3, 231).
α' -Bromo- α -methylcamphor.....	0.7604 : 1 : 0.4921 (Minguin, <i>Compt. rend.</i> , 1903, 136, 752).

Multiplying a by 2 and c by 4, we obtain the axial ratios for the latter compound: 1.5208 : 1 : 1.9684.

It seems therefore that α' -bromo- α -methylcamphor belongs to the isomorphous series the existence of which was first pointed out by Lowry (*Trans.*, 1898, 73, 574):

$\alpha\alpha'$ -Dibromocamphor.....	1.5778 : 1 : 2.0685
α' -Chloro- α -bromocamphor	1.5395 : 1 : 1.9144
α -Chloro- α' -bromocamphor	1.5338 : 1 : 1.9020
$\alpha\alpha'$ -Dichlorocamphor	1.4820 : 1 : 1.8358
α' -Bromo- α -methylcamphor.....	{1.5208 : 1 : 1.9684}

EXPERIMENTAL.

α -Methylcamphor was first prepared by Minguin (*Compt. rend.*, 1891, 112, 1370) from methyl α -methylcamphor- α' -carboxylate. Since this method of preparation, commencing with camphor, necessitates the preparation of three intermediate compounds, attempts were made at the beginning of the investigation to synthesise this compound directly

from camphor by acting on the sodium derivative of the latter with methyl iodide.

Finely powdered sodamide was added to a solution of camphor in dry benzene in a flask fitted with a reflux condenser and the mixture heated until ammonia ceased to be evolved. Methyl iodide was then added very cautiously to the sodium camphor so obtained and the whole heated for some time; the product was shaken several times with water to remove the sodium bromide and then repeatedly extracted with a mixture of four parts of concentrated sulphuric acid with one part of water. On pouring the acid extract into water, an oil was precipitated; this was separated by steam distillation from the acid liquid, dried, and fractionally distilled. The chief fraction passed over between 215–218°; it solidified after some time at about 10°.

Since α -methylcamphor boils at 220°, it was evident that this fraction was not pure α -methylcamphor but probably a mixture of this compound with unchanged camphor. As it was impossible by mere fractional distillation to effect a separation of the two substances, it was decided to brominate the mixture and submit the product to fractional crystallisation so as to obtain α' -bromo- α -methylcamphor, from which pure α -methylcamphor could be prepared by treatment with zinc dust in alcoholic solution.

The fraction boiling at 215–218° was therefore heated in a flask on a water-bath and bromine added, drop by drop, slightly in excess of the quantity required by theory. The mixture having been heated until hydrogen bromide ceased to be evolved was shaken with a dilute solution of sodium hydroxide and the pasty mass so obtained fractionally distilled in steam. The solid product was purified by crystallisation from alcohol and then from light petroleum, from which solvent it crystallised in large prisms melting at 62°. It was at first thought that this product was α' -bromo- α -methylcamphor, which according to Minguin (*Compt. rend.*, 1903, 136, 752) melts at 61°. However, on analysis, this was found not to be the case:

- I. 0.2303 gave 0.1986 AgBr. Br = 36.70.
 - II. 0.1768 „ 0.1524 AgBr. Br = 36.68.
- $C_{11}H_{17}OBr$ requires Br = 32.65 per cent.

The substance was then recrystallised three times from light petroleum and again analysed:

- I. 0.1871 gave 0.1621 AgBr. Br = 36.87.
- II. 0.1790 „ 0.1550 AgBr. Br = 36.85.

From these results, it is clear that the composition of the substance had undergone no change during the recrystallisation. The observed rotation of an ethyl-alcoholic solution containing 0.7542 gram per 15 c.c. of solution in a 2-dem. tube at 20° was +14.64°, whence

$[\alpha]_D^{25} + 145.4^\circ$. The specific rotatory power of α' -bromo- α -methylcamphor is $[\alpha]_D^{25} + 184.4^\circ$. Now if the substance were an impure α' -bromo- α -methylcamphor, it follows from these figures that the impurity must have been one containing more bromine and of smaller specific rotatory power than this compound. Since $\alpha\alpha'$ -dibromocamphor melts at 61° and has the specific rotatory power $[\alpha]_D^{25} + 40^\circ$, it was thought probable that the impurity might be $\alpha\alpha'$ -dibromocamphor. Some of the substance was therefore mixed with a little $\alpha\alpha'$ -dibromocamphor and the melting point of the mixture determined; it was found to be 61° . This result tends to show the correctness of the conclusion; it may here be mentioned that subsequently, when the substance containing 36.7 per cent. of bromine was heated with a large excess of alcoholic potash, not only was methylenecamphor obtained but also α -bromocamphor, m. p. 76° derived from the $\alpha\alpha'$ -dibromocamphor present. An attempt was made to obtain pure α' -bromo- α -methylcamphor from the mixture by treatment with small quantities of alcoholic potash, the object being to convert the $\alpha\alpha'$ -dibromocamphor into α -bromocamphor and by fractional crystallisation to separate this compound from the α' -bromo- α -methylcamphor; but this was not a success.

Hydrolysis of Methyl α -Methylcamphor- α' -carboxylate.

Since pure α -methylcamphor could not be obtained directly from camphor, it was prepared by hydrolysing methyl α -methylcamphor- α' -carboxylate. Brühl (*Ber.*, 1902, 35, 3623) has shown that when a mixture of this ester with five times its weight of 15 per cent. sodium methoxide in methyl alcohol is heated for about four hours at 80° , it is completely hydrolysed, α -methylcamphor- α' -carboxylic acid being formed together with some α -methylcamphor. It seemed probable, therefore, that a complete conversion into α -methylcamphor would be effected by prolonged heating, and that the rather objectionable method originally used by Minguin, namely, treatment of the ester with alcoholic potash in sealed tube at 120 — 130° for twelve hours, might be dispensed with. However, it was found that even after heating the ester with sodium methoxide on a water-bath during twenty-four hours only about one-half had been converted into α -methylcamphor, so it was decided to use alcoholic potash as the hydrolysing agent and an autoclave instead of sealed tubes.

A flask containing 110 grams of the ester dissolved in about 400 c.c. of 95 per cent. ethyl alcohol, to which had been added a solution of 60 grams of potassium hydroxide in 50 c.c. of water, was placed in an autoclave; this was heated in an oil-bath the temperature of which was maintained at 160 — 170° during about twelve hours. The liquid in the flask was then poured into a fairly

large quantity of water, the α -methylcamphor was extracted with ether and the ethereal solution dried and fractionally distilled. At first ether and alcohol passed over, after which were obtained the following fractions: I. $216-220^\circ = 16$ grams. II. $222-223^\circ = 26$ grams. III. $223-233 = 15.5$ grams. Refractionation yielded a fraction boiling at $220-221^\circ$, which solidified on cooling to a crystalline solid melting at $37-38$, the temperature given by Minguin. Further purification may be effected by diluting a 5 per cent. alcoholic solution with a moderately large bulk of water; the α -methylcamphor separates from the diluted alcohol in white, glistening leaflets melting at $38-39^\circ$. An ethyl-alcoholic solution of the compound containing 5 grams per 100 c.c. of solution gave $[\alpha]_D^{25} + 30.0^\circ$. Minguin in his first communication on α -methylcamphor (*Compt. rend.*, 1891, 112, 1370) gives $[\alpha]_D + 270.65^\circ$ (1.66 grams per 10 c.c.), which value is that quoted in all text-books. Subsequently (*Compt. rend.*, 1903, 136, 752) he gives the value $[\alpha]_D + 27.65^\circ$. The addition of sodium ethoxide to the alcoholic solution of α -methylcamphor is unaccompanied by any change in the specific rotatory power of the solution, so that, although still containing a hydrogen atom in the α -position, α -methylcamphor is apparently not converted into its stereoisomeride under the influence of sodium ethoxide.

α' -Bromo- α -methylcamphor.

This compound, originally obtained by Minguin by treating α -methylcamphor dissolved in carbon disulphide with bromine, is more readily prepared by gradually adding the theoretical quantity of bromine to the alkylcamphor contained in a flask heated on a water-bath. When hydrogen bromide ceases to be evolved, the crude product is washed with dilute sodium hydroxide and recrystallised several times from hot alcohol, from which it separates in crystals melting at 62.5° (Minguin gives 61°) and resembling ammonium chloride. A mixture of four parts of this compound with one part of $\alpha\alpha'$ -dibromocamphor (m. p. 61°) was found to melt at $60-61.5^\circ$, so that the conclusion arrived at above with reference to the compound obtained by the bromination of the mixture of camphor and α -methylcamphor receives additional support:

0.1864 gave 0.1438 AgBr; Br = 32.82.

0.1510 „ 0.1154 AgBr; Br = 32.52.

$C_{11}H_{17}OBr$ requires Br = 32.65 per cent.

The specific rotatory power was determined in 99.5 per cent. ethyl-alcoholic solution, the concentration being 5 grams per 100 c.c.; the value obtained was $[\alpha]_D^{25} + 184.4^\circ$ (Minguin gives $[\alpha]_D + 176.8^\circ$). The specific rotatory power twenty hours after the addition of sodium ethoxide to make the solution approximately $N/1000$ was

$[\alpha]_D^{20} + 184.1^\circ$; in other words, α' -bromo- α -methylcamphor undergoes no stereoisomeric change in the presence of traces of sodium ethoxide. Similarly, a benzene solution containing 0.6966 gram per 15 c.c. of solution was examined in a 2-dm. tube at 25° . The rotation observed was $+17.73^\circ$, whence $[\alpha]_D^{20} + 190.8^\circ$. One drop of piperidine was then added to the contents of the tube; the rotation observed twenty-four hours after the addition of the base was $+17.70^\circ$, so that no isomeric change had been produced by the presence of this base.

ω -Bromo- α -methylcamphor.

This isomeride of the compound just described is prepared by the addition of hydrogen bromide to methylenecamphor. The latter compound is obtained by boiling for sixteen hours a solution of 30 grams of α' -bromo- α -methylcamphor in 140 c.c. of alcohol with 30 grams of potassium hydroxide dissolved in an equal weight of water. The brown solution thus obtained is diluted with water, distilled in steam, the distillate extracted with ether, and the ethereal solution dried and then fractionally distilled. The portion which passes over between 216° and 219° (10 grams) is practically pure methylenecamphor.

In order to bring about the interaction of hydrogen bromide and methylenecamphor, the latter compound is dissolved in about three times its weight of a cold saturated solution of hydrogen bromide in glacial acetic acid and the mixture allowed to stand in a stoppered bottle at the ordinary temperature for at least six weeks. At the end of this period, the light brown solution is diluted with a large volume of water, the heavy oil which separates is washed with dilute sodium hydroxide and the pasty mass so obtained washed thoroughly with water and dried on a porous plate. The crude product is best purified by crystallisation from alcohol, from which solvent it crystallises in colourless prisms melting at $65-66^\circ$:

0.1444 gave 0.1116 AgBr. Br = 32.88.

0.1734 „ 0.1330 AgBr. Br = 32.64.

$C_{11}H_{17}OBr$ requires Br = 32.65 per cent.

The specific rotatory power was determined in 99.5 per cent. ethyl-alcoholic solution containing 5 grams per 100 c.c. The value obtained was $[\alpha]_D^{20} + 155.4^\circ$; Minguin gives $[\alpha]_D + 150.5^\circ$.

The specific rotatory power twenty hours after the addition of sodium ethoxide to render the solution approximately $N/1000$ was $[\alpha]_D^{20} + 155.2^\circ$, so that this compound also appears to undergo no stereoisomeric change in the presence of sodium ethoxide. With the object of confirming this result, a benzene solution containing 0.57 gram per 15 c.c. of solution was examined in a 2-dm. tube at 25° . The rotation observed was $+10.08^\circ$, whence $[\alpha]_D^{20} + 132.6^\circ$. One hour

after the addition of a drop of piperidine to the contents of the tube, the observed rotation was $+10.1^\circ$; the rotation twenty-four hours after the addition of the base could not be accurately determined, owing to the separation of fine needle-shaped crystals of piperidine hydrobromide; however, no very marked change in the rotatory power could be detected.

The fact that the addition of alkali to the solution had no effect on the optical rotatory power seemed to support the suggestion that this compound is an α' -bromo- α -methylcamphor; in other words, a stereoisomeride of the compound melting at 62.5° . Further investigation, however, proved this to be incorrect.

Action of Potassium Permanganate and Nitric Acid on the Isomeric Monobromo-derivatives of α -Methylcamphor.

The two isomerides were treated under exactly identical conditions with equal volumes of an aqueous solution of potassium permanganate; although both remained practically unaffected by this agent even after very prolonged heating, nevertheless it was observed that the colour of the permanganate was discharged quicker and more bromide was found in solution in the case of the isomeride melting at $65-66^\circ$ than in that melting at 62.5° .

A still greater difference was observed in the behaviour of these substances towards concentrated nitric acid (sp. gr. 1.42). When the isomeride melting at 62.5° is added to nitric acid containing in suspension some finely-divided silver nitrate, it at once becomes oily and almost immediately a dense, yellow precipitate of silver bromide appears the quantity of which increases considerably on standing. On the other hand, the isomeride melting at $65-66^\circ$ does not give a precipitate of silver bromide when similarly treated and may be recovered unchanged even after standing some days in contact with the acid. This result tends to confirm Minguin's conclusions, since it is to be expected that α' -bromo- α -methylcamphor melting at 62.5° would lose bromine more readily than ω -bromo- α -methylcamphor melting at $65-66^\circ$.

A yellow oil slightly denser than water was obtained by steam distillation from the product of the interaction of α' -bromo- α -methylcamphor and nitric acid; as the quantity was small, it was not further investigated; it was in all probability an α' -nitro- α -methylcamphor.

Action of Bromine on the Isomerides. Preparation of ω,ω' -Dibromo- α -methylcamphor, $C_{10}H_{16}Br(OH_2Br)O$.

When a mixture in equimolecular proportions of the compound melting at $65-66^\circ$ and bromine is heated on a water-bath, hydrogen bromide is evolved, the mixture becoming almost colourless. The

rude substance thus obtained, after washing with dilute sodium hydroxide and finally with water, is readily purified by crystallisation from hot alcohol, from which solvent it is obtained in long, slender, colourless, silky needles melting at $108-109^{\circ}$. The compound thus formed is a dibromo-derivative of α -methylcamphor:

0.1430 gave 0.1663 AgBr. Br = 49.49.

0.1604 " 0.1865 AgBr. Br = 49.48.

$C_{11}H_{16}OBr_2$ requires Br = 49.35 per cent.

When similarly treated with bromine, the isomeride melting at 62.5° remains unattacked; there is therefore little doubt that this compound is α -bromo- α -methylcamphor, whilst the isomeride melting at $65-66^{\circ}$ is ω -bromo- α -methylcamphor.

That the above dibromo-derivative of α -methylcamphor is undoubtedly ω - α' -dibromo- α -methylcamphor follows from the fact that the same compound is produced by the addition of bromine to methylenecamphor. When the latter compound is mixed with the theoretical quantity of bromine, it is at once evident that interaction has taken place, since heat is generated and the colour of the halogen slowly disappears. After two or three crystallisations from hot spirit, the product melts at 108° ; a mixture of this substance with that obtained by brominating ω -bromo- α -methylcamphor melts at 108° .

ω - α' -Dibromo- α -methylcamphor is only moderately soluble in cold alcohol or light petroleum but is readily so in benzene, from which it crystallises in stout, colourless prisms.

For the determination of the rotatory power, a benzene solution containing 0.715 gram per 15 c.c. of solution was examined in a 2-dm. tube at 20° . The rotation observed was $+11.203^{\circ}$, whence $[\alpha]_D^{20} + 117.5^{\circ}$.

α -Methylcamphor- β -sulphonic Acid.

This acid is obtained quite readily from α -methylcamphor by the method originally described by Reychler (*Bull. Soc. chim.*, 1898, 19, [iii], 120). A mixture of acetic anhydride and sulphuric acid is prepared by cautiously adding two parts by weight of the latter compound to four parts by weight of the former and to the mixture is added three parts of α -methylcamphor. The slightly brown solution, after standing several days in the cold, deposits large, transparent crystals of the sulphonic acid; if, however, a little of the solid acid be added to the mixture even after standing only twenty-four hours, a copious separation of the sulphonic acid at once takes place. When no more sulphonic acid separates out, the liquid is allowed to drain away from the crystalline mass, which is then washed two or three times with small quantities of glacial acetic acid and finally purified by recrystallisation from hot ethyl acetate. The sulphonic acid remaining in the

acid mother-liquor may be separated by boiling the diluted mixture several hours with animal charcoal until practically the whole of the acetic acid has been volatilised, when the liquid is filtered and neutralised with barium carbonate. The barium salt separates from the filtered solution when sufficiently concentrated and is best purified by recrystallisation from water.

α -Methylcamphor- β -sulphonic acid crystallises from hot ethyl acetate in large, transparent prisms, which quickly become opaque when removed from the solution. It is an exceedingly deliquescent substance, which melts at 114 — 116° but is decomposed; it dissolves readily in cold water and hot glacial acetic acid or ethyl acetate. The observed rotatory power of an aqueous solution containing 0.7608 gram per 15 c.c. of solution in a 2 -dcm. tube at 20° was $+1.897^\circ$, whence $[\alpha]_D^{20} + 18.7^\circ$.

Barium α -methylcamphor- β -sulphonate, $(C_{11}H_{17}O_4S)_2Ba \cdot 6H_2O$, crystallises from hot aqueous solutions of suitable concentration in large, stout, transparent, hexagonal plates, which melt in their water of crystallisation at 66° . The salt parts with the whole of its water of crystallisation when kept in a desiccator over concentrated sulphuric acid for two or three days:

0.5740 gave 0.1770 $BaSO_4$. $Ba = 18.15$. 0.4950 gave 0.1536 $BaSO_4$. $Ba = 18.26$. 0.5628 gave 0.1740 $BaSO_4$. $Ba = 18.20$.

0.4260 lost 0.0626 H_2O . $H_2O = 14.69$. 0.5982 lost 0.0889 H_2O . $H_2O = 14.86$. 0.4954 lost 0.0750 H_2O . $H_2O = 15.13$.

$(C_{11}H_{17}O_4S)_2Ba \cdot 6H_2O$ requires $Ba = 18.68$; $H_2O = 14.69$ per cent.

The potassium salt could not be obtained in a crystalline form; an aqueous solution evaporated on a water-bath leaves a somewhat gelatinous residue, which becomes quite hard and brittle on standing a few days in a vacuum desiccator over sulphuric acid.

α -Methylcamphor- β -sulphonyl chloride, $C_{11}H_{17}O \cdot SO_2Cl$, is prepared by rubbing together phosphorus pentachloride and a slight excess of the anhydrous potassium sulphonate. The semi-solid mixture is allowed to stand for two or three hours and then poured on to, and intimately ground up with, a large quantity of finely-powdered ice, after which the solid sulphonyl chloride is collected, washed well with ice-water, and dried in a vacuum desiccator. The crude substance is purified by crystallisation from light petroleum at temperatures below 10° :

0.1972 gave 0.1054 $AgCl$. $Cl = 13.20$.

0.3366 „ 0.1798 $AgCl$. $Cl = 13.19$.

$C_{11}H_{17}O_2ClS$ requires $Cl = 13.39$ per cent.

The sulphonyl chloride crystallises in transparent, prismatic needles, which melt at 33° ; it is a fairly stable substance which is readily dis-

solved by most organic solvents. The observed rotation of a 5 per cent. solution in benzene in a 2-dcm. tube was $+2.95^\circ$, whence $[\alpha]_D^{20} + 29.5^\circ$.

α -Methylcamphor- β -sulphonamide, $C_{11}H_{17}O \cdot SO_2 \cdot NH_2$, is obtained when the sulphonyl chloride is treated with a concentrated aqueous solution of ammonia. To separate it from any anhydramide which may possibly be formed at the same time, it was crystallised twice from hot water—in which the anhydramide is only very sparingly soluble—and finally from either hot alcohol or benzene:

0.2372 gave 11.65 c.c. N_2 (dry) at 12.5° and 756 mm. $N = 5.86$.

0.1898 " 9.35 c.c. " " 13.5° " 749.2 mm. $N = 5.80$.

$C_{11}H_{15}O_2NS$ requires $N = 5.72$ per cent.

The sulphonamide crystallises from hot water in long, silky needles, and from hot alcohol in transparent prisms, which melt at 150° . Unlike camphor- β -sulphonamide, it does not lose water when heated above its melting point and may even be heated to 200° without undergoing decomposition.

The observed rotation effected by a chloroform solution containing 0.376 gram per 15 c.c. of solution in a 2-dcm. tube at 20° was -0.316° , whence $[\alpha]_D^{20} - 6.3^\circ$.

α -Methylcamphor- β -sulphonanhydramide.—As was first observed by Lowry (Trans, 1902, 81, 1448), camphor- β -sulphonamide when covered with a concentrated solution of hydrogen chloride quickly dissolves and in a few minutes the anhydramide separates from the solution. The behaviour of α -methylcamphor- β -sulphonamide towards the acid is somewhat similar, although in this case it is necessary to heat the acid in order to dissolve the sulphonamide.

The anhydramide separates very slowly from the solution so obtained on standing:

0.1918 gave 10 c.c. N_2 (dry) at 17° and 754.2 mm. $N = 6.11$.

0.1900 " 10.1 c.c. " " 15° " 746 mm. $N = 6.20$.

$C_{11}H_{15}O_2NS$ requires $N = 6.16$ per cent.

The anhydramide is practically insoluble in cold water and alcohol, sparingly soluble in hot alcohol. It separates from a solution in hot alcohol as a fine crystalline powder, which melts at 167.5° .

β -Bromo- α -methylcamphor, $C_{11}H_{17}OBr$, is formed when α -methylcamphor- β -sulphonyl bromide is heated, sulphur dioxide being simultaneously evolved. The sulphonyl bromide, prepared by the interaction of phosphorus pentabromide and the anhydrous potassium sulphonate, could not be obtained in the solid state, so the oily substance was dissolved in dry xylene and the solution boiled in a flask, fitted with a reflux condenser, for about twelve hours. At the end of this period, sulphur dioxide had ceased to be evolved, so the resulting solution

of β -bromo- α -methylcamphor was submitted to fractional steam distillation. At first, practically only xylene passed over with the water vapour but towards the end of the distillation an oil passed over which was heavier than water. On standing, traces of xylene present in the oil evaporated off and left a solid which crystallised from dilute alcohol in silky needles melting at 55° .

0.1180 gave 0.0908 AgBr. Br = 32.74.

$C_{11}H_{17}OBr$ requires Br = 32.65 per cent.

The observed rotation effected by an ethyl-alcoholic solution containing 0.2586 gram per 15 c.c. of solution in a 2-dm. tube at 25° was $+0.65^{\circ}$; whence $[\alpha]_D^{25} + 18.8^{\circ}$. The specific rotatory power twenty-four hours after the addition of sodium ethoxide to render the solution approximately $N/100$ was $[\alpha]_D^{25} + 18.0^{\circ}$. It is therefore evident that β -bromo- α -methylcamphor is not converted into β -bromo- α' -methylcamphor under the influence of sodium ethoxide. β -Bromo- α -methylcamphor is extremely soluble in the common organic solvents.

α -Methylcamphoroxime, $C_{11}H_{18}NOH$.

α -Methylcamphor yields an oxime but not quite so readily as camphor. It may be prepared as follows: A solution of 20 grams of hydroxylamine hydrochloride in an equal weight of hot water is added to a solution of 11 grams of α -methylcamphor in 150 c.c. of alcohol and to the mixture is added 12 grams of finely-powdered potassium carbonate. The mixture is kept at the ordinary temperature for a day, then heated to boiling and again kept at the ordinary temperature for several days, after which it is diluted considerably with water and the viscid oil which separates submitted to fractional steam distillation. At first, an oil passes over with the water vapour but after some time a very viscid oil distils over, which solidifies very slowly on standing. This crude material is purified with some difficulty by repeated crystallisation from dilute alcohol (1:1), from which it separates in crystals resembling ammonium chloride; from more dilute alcohol, it crystallises in long, slender needles melting at 55° :

0.2002 gave 13.65 c.c. N_2 (dry) at 23° and 745 mm. $N = 7.77$.

0.1506, " 10.3 c.c. " " 19° " 753 mm. $N = 7.94$.

$C_{11}H_{19}ON$ requires $N = 7.73$ per cent.

α -Methylcamphoroxime possesses a strong camphor-like odour, is extremely soluble in all common organic solvents, but unlike camphoroxime, it does not dissolve in aqueous alkalis.

The specific rotatory power was determined in 99.5 per cent. ethyl-alcoholic solution. The values obtained were $[\alpha]_D^{25} + 30.3^{\circ}$ (5 grams per 100 c.c. of solution) and $[\alpha]_D^{25} + 32.0^{\circ}$ (2.5 grams per 100 c.c. of solution).

The Hydrochloride.—When dry hydrogen chloride is passed into a solution of the oxime in dry ether, a copious precipitate of the *hydrochloride* is obtained in silky needles. It melts but undergoes decomposition at 138° and is hydrolysed by water:

0.1692 required 7.45 c.c. of $N/10$ KOH. $HCl = 16.05$.

$C_{11}H_{19}ONCl$ requires $HCl = 16.75$ per cent.

α -Methylcamphoroxime dissolves in warm dilute sulphuric acid, forming a clear solution, which, however, when heated to boiling, quickly becomes turbid, owing to the separation of a pleasant smelling oil. This was separated from the dilute acid by steam distillation, dried and fractionally distilled. The principal fraction, which passes over between 226° and 228°, is a colourless oil possessing a somewhat peppermint-like odour. From its mode of formation, it is in all probability *methylcampholanonitrile*, produced by the dehydration of the oxime by the dilute sulphuric acid, since, when boiled with alcoholic potash, ammonia is slowly evolved. The acid formed by the hydrolysis of the nitrile has not yet been investigated.

In conclusion, the author desires to express his thanks to Professor H. E. Armstrong for suggesting this work, and for the valuable advice he has given him in carrying it out.

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CXXIV.—*Viscosity Determinations at High Temperatures.*

By CHARLES EDWARD FAWSITT.

The experimental determination of the viscosity of liquids at high temperatures constitutes rather a difficult problem. That this subject should have been so much avoided hitherto is to be regretted, as, apart from the stoicheiometrical relations involved, the bearing of this property on crystallisation deserves close examination. In the present communication the results from the examination of some fused salts and metals are submitted.

A few determinations of viscosity at high temperatures have already been carried out. Koch (*Wied. Annalen*, 1881, 14, 1) has determined the viscosity of mercury over a large range of temperature. Beck (*Zeitsch. physikal. Chem.*, 1907, 58, 423) has determined the viscosity of mercuric bromide and iodide. Lorenz and Kalmus (*Zeitsch. physikal. Chem.*, 1907, 59, 214) have determined the viscosity of five

fused salts. Goodwin and Mailey (*Phys. Review*, 1908, 26, 28) have worked on the viscosity of a number of nitrates, and have also determined their electrical conductivities. All these results are confined to temperatures below 600°, and the experimenters were able to use the capillary method in all cases. Some interesting measurements at higher temperatures have been made on silicates by Doelter (*Sitzungsber. K. Akad. Wien*, 1905, 114, 529), and Arndt (*Zeitsch. Elektrochem.*, 1907, 13, 578) has determined the viscosity of sodium metaphosphate and boric anhydride. The two last-named experimenters have worked with liquids of very high viscosity, and their methods of experiment are of no use for the determination of the viscosity of fused metals or of the majority of salts, as these have a relatively low viscosity.

Method.—In a communication recently published (*Proc. Roy. Soc.*, 1908, 80, A, 290) the author has given a general description of a method devised more especially for the determination of the viscosity of fused metals and salts. In this method a small disk of iron, platinum, or fireclay is allowed to oscillate torsionally in the liquid, the viscosity of which is to be determined. From the observations it is possible to calculate the logarithmic decrement of the amplitude, and from this the viscosity of the liquid, provided its density is known. The apparatus is standardised in three liquids of known viscosity and density. Having standardised the apparatus, it is advisable to test it in a further number of liquids of known viscosity in order to find what degree of accuracy is obtainable. It was found that with a disk of 26–29 mm. diameter, the accuracy obtainable could be taken as ± 2 per cent. In using the disk at high temperatures, a small correction for its expansion is made. The disk is attached at its centre to a thin rod, which at its upper end is attached to a copper suspension wire. The wire used in these experiments was about one metre long, and the period of oscillation of the apparatus about eight seconds. The period was practically identical in all the liquids examined. The apparatus was first of all allowed to swing in air and the logarithmic decrement noted. It was then allowed to swing in the three standardising liquids. These should be chosen so that one at least of them has a viscosity and density near to the viscosity and density of the liquid, the viscosity of which is to be determined. When working with salts, the three liquids used were water, chloroform, and fused sodium nitrate. When working with metals, mercury, chloroform, and isobutyl alcohol were taken.

Whilst this method appears at first sight to have great simplicity, its application is nevertheless attended with some difficulties. The difficulties are due to errors caused by impurities on the surface of the liquid. When the disk is allowed to sink into the liquid, the only

part of the apparatus which comes in contact with the surface is the relatively thin stem. The diameter of the stem was 2 mm., and it might be imagined that the impeding action of any surface impurity on this would be so slight as to be negligible. That is, however, not so; the surface of any liquid, and more especially the surface of a metal (even if non-oxidisable), is liable to have its surface skin rendered very viscous, although no visible impurity is present. The cause of this is undoubtedly the presence of some dust or dirt in an amount too small to be visible. The errors caused by such impurities easily amount to 10 per cent. When any visible impurity is present on the surface, experiment is hopeless. When every care is taken to prepare mercury pure and clean, the surface skin is not any more viscous than any layer in the interior. But if it be allowed simply to stand, it will soon become much more viscous. The most satisfactory method of experiment with mercury or any other metal is to cover the surface with another liquid. In the case of mercury, it will be found that a thin layer of very dilute nitric acid keeps the surface in good condition. Below 270° (molten tin), it is possible to get a good, clean surface by covering with melted resin. From 270° upwards for about two hundred degrees, a cover of zinc and ammonium chlorides answers well. At higher temperatures, the only cover which gave any results was borax. Attempts were made to keep the surface of oxidisable metals clean by filtering them and then keeping them in an atmosphere of carbon dioxide; in all cases, however, a very small amount of oxygen leaked in, and this sufficed to spoil the results. It is undoubtedly best to use a cover of some kind.

In the experiments with both metals and salts, a large number of observations were made at each temperature given. As all the errors are in the direction of producing results that are too high, the lowest results have always been considered the correct ones, and the numbers for viscosity given here are the lowest results obtained in each case.

The experiments give the logarithmic decrement of the amplitude, and from this the viscosity is obtained by the formula

$$\lambda - \lambda_0 = c_1 \sqrt{\mu d} + c_2 \mu + c_3 \mu d,$$

where λ is the logarithmic decrement for the liquid experimented on,

λ_0 is the logarithmic decrement for air,

μ is the viscosity of the liquid, and d its density.

c_1, c_2, c_3 are constants, and are obtained by experimenting with liquids of known viscosity.

The calculations thus involve the solution of three (linear) simultaneous equations and the subsequent solution of a quadratic equation.

The numbers in the density column were obtained in the case of the metals and sodium chloride from Landolt and Börnstein's *Tabellen* (1905). The other numbers were obtained by experiment. The method used was that of sinking a ball of platinum in the fused liquid and noting the consequent loss of weight. Temperature was measured by a platinum and platinum-rhodium thermo-couple connected to a Siemens-Halske galvanometer. The readings may be taken as correct to $\pm 5^\circ$. The viscosities are given in absolute (C.G.S.) units.

Viscosity Measurements on Fused Salts.

These measurements were carried out partly from the interest which attaches to them on their own account, but also because it was tolerably certain that in the case of viscosity, as with other properties, relations obtainable with fused salts would have their parallel in the case of metals. The following salts were examined more particularly: sodium and potassium nitrates, sodium, potassium, and lithium chlorides, and sodium and potassium bromides; also mixtures of sodium nitrate and potassium nitrate. The results are contained in the following tables:

TABLE I.

Sodium Nitrate; m. p. 308° .

Temperature.	Density.	Viscosity.
324°	1.903	0.0271
333	1.899	0.0256
353	1.887	0.0235
393	1.860	0.0200

TABLE II.

Potassium Nitrate; m. p. 330° .

Temperature.	Density.	Viscosity.
349°	1.863	0.0267
362	1.850	0.0249
383	1.833	0.0225
397	1.824	0.0214
407	1.815	0.0209

TABLE III.

Sodium Chloride; m. p. 822° .

Temperature.	Density.	Viscosity.
841°	1.559	0.0130
859	1.529	0.0120
896	1.500	0.0101
924	1.486	0.0097

TABLE IV.

Potassium Chloride; m. p. 782° .

Temperature.	Density.	Viscosity.
799°	1.520	0.0142
835	1.490	0.0121
929	1.438	0.0099
1055	1.370	0.0061

TABLE V.

Sodium Bromide; m. p. 757° .

Temperature.	Density.	Viscosity.
762°	2.324	0.0142
766	2.316	0.0135
789	2.308	0.0128
880	2.220	0.0109

TABLE VI.

Potassium Bromide; m. p. 744° .

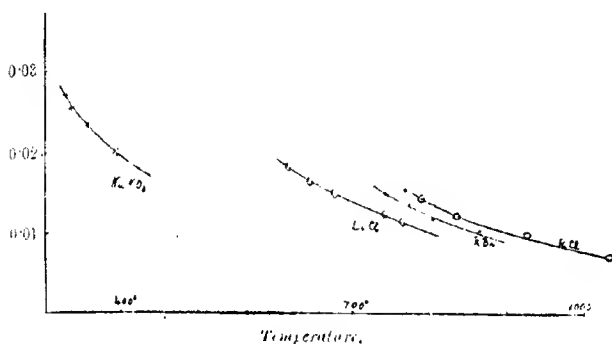
Temperature.	Density.	Viscosity.
745°	2.110	0.0148
775	2.087	0.0134
805	2.063	0.0119
862	2.023	0.0105

TABLE VII.
Lithium Chloride; m. p. 605°.

Temperature.	Density.	Viscosity.
617°	1.475	0.0181
645	1.462	0.0164
675	1.450	0.0149
742	1.426	0.0125
765	1.417	0.0111

The results for sodium nitrate, potassium and lithium chlorides, and potassium bromide are plotted in Fig. 1. If the salts are compared

FIG. 1.



at temperatures 20° above the respective melting points, the following results are obtained:

TABLE VIII.

Substance.	Temperature.	Viscosity.
NaNO ₃	328°	0.0262
KNO ₃	359	0.0251
NaCl.....	812	0.0128
KCl.....	802	0.0133
NaBr.....	777	0.0130
KBr.....	761	0.0137
LiCl.....	625	0.0176

The first thing noticeable about these results is that the substances have a relatively small viscosity; the viscosity of water at 20° is 0.0102. Secondly, it will be noticed that the viscosities of the potassium and sodium salts are nearly the same in each case. The lithium salt is noticeably more viscous than the corresponding potassium salt. Goodwin and Mailey (*loc. cit.*) found that lithium nitrate was more viscous than potassium nitrate. Some other salts were examined besides those reported. Zinc chloride and borax, for example, were

found to be very viscous, of the same order of viscosity as rape oil. These, however, are undoubtedly exceptional; and it appears that the majority of fused salts have a small viscosity.

Mixtures of Salts.

Mixtures of sodium and potassium nitrates were examined, and the observations in all cases were continued to as near the melting point as possible. The proportions in the mixtures are expressed in percentage by weight.

TABLE IX.

Sodium Nitrate (80) and Potassium Nitrate (20); m. p. 278°.

Temperature.	Density.	Viscosity.
278°	1.930	0.0325
328	1.894	0.0248
344	1.884	0.0234
373	1.864	0.0217

TABLE X.

Sodium Nitrate (60) and Potassium Nitrate (40); m. p. 240°.

Temperature.	Density.	Viscosity.
262°	1.938	0.0368
276	1.928	0.0324
316	1.897	0.0247
332	1.883	0.0237

TABLE XI.

Sodium Nitrate (45.5) and Potassium Nitrate (54.5); m. p. 224°.

Temperature.	Density.	Viscosity.
229°	1.963	0.0170
236	1.957	0.0446
269	1.934	0.0331
286	1.920	0.0296
291	1.914	0.0287
309	1.902	0.0266
331	1.881	0.0217
346	1.873	0.0238

TABLE XII.

Sodium Nitrate (35) and Potassium Nitrate (65); m. p. 237°.

Temperature.	Density.	Viscosity.
215°	1.943	0.0423
253	1.936	0.0405
289	1.907	0.0396
340	1.870	0.0246

TABLE XIII.

Sodium Nitrate (24) and Potassium Nitrate (76); m. p. 263°.

Temperature.	Density.	Viscosity.
276°	1.920	0.0338
326	1.880	0.0259
335	1.873	0.0242

The melting-point curve for mixtures of sodium and potassium nitrates has already been studied by Carveth (*J. Physical Chem.*, 1898, 2, 209), and the eutectic point was found to exist at the composition 45.5 per cent. of sodium nitrate and 54.5 per cent. of potassium nitrate. If the viscosities of the mixtures at temperatures 20° above the melting points are taken for comparison, the following numbers are obtained:

TABLE XIV.

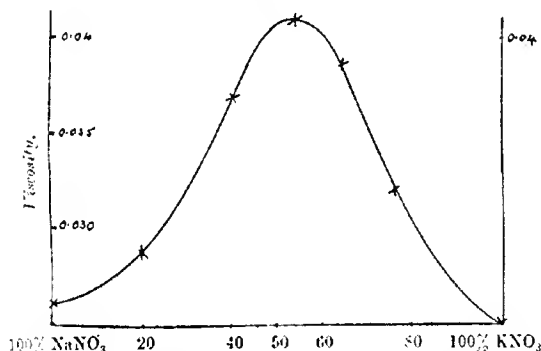
Composition per cent.		Temperature.	Viscosity.
NaNO ₃ .	KNO ₃ .		
100	0	323°	0.0262
80	20	298	0.0287
60	40	260	0.0370
45.5	54.5	244	0.0410
35	65	257	0.0387
24	76	283	0.0322
0	100	359	0.0250

These results are shown graphically in Fig. 2.

There is a distinct maximum at the composition represented by the eutectic mixture.

It is also of interest here to consider the viscosities at temperatures

FIG. 2.



linearly situated between 308° and 339°, the melting points of the (pure) components. As the viscosities of sodium nitrate and potassium nitrate at their melting points are almost the same, it might be expected that the viscosities of all the mixtures would also be the same if compared at temperatures linearly situated between the melting points of the components.

TABLE XV.

Composition per cent.		Temperature.	Viscosity.
NaNO ₃ .	KNO ₃ .		
100	0	308°	0.0296
80	20	314	0.0266
60	40	320	0.0244
45.5	54.5	324	0.0252
35	65	327	0.0255
24	76	331	0.0250
0	100	339	0.0283

There is a distinct decrease in the viscosity when the two salts are mixed. The fall is probably connected with a change in the dissociation caused by the mixing of the salts.

The Variation of Viscosity with Temperature.

The viscosity of a salt diminishes with rising temperature; the change is more rapid at first than afterwards. Comparing different salts, it will be noticed that those which have the greater viscosity at their melting points are also those whose viscosity falls most rapidly with rising temperature. This matter may be best discussed by considering in each case the fall of viscosity for equal intervals of temperature measured from the melting point, or a temperature equally distant from the melting point. Take, for example, in each case, the viscosity at 20° and at 70° above the melting point; let these be denoted by μ_{20} and μ_{70} respectively; let μ_a be the average viscosity throughout the interval. Then $\frac{\mu_{70} - \mu_{20}}{\mu_a}$, which is proportional to the temperature coefficient, should be a comparable function for different salts.

In the following table, the values of $\frac{\mu_{70} - \mu_{20}}{\mu_a}$ for a number of the substances are given, also the quotients of this function by μ_a .

TABLE XVI.

Substance.	μ_a	$\frac{\mu_{70} - \mu_{20}}{\mu_a}$	$\frac{\mu_{70} - \mu_{20}}{(\mu_a)^2}$
KNO ₃	0.0226	0.212	9.4
NaNO ₃	0.0236	0.220	9.3
45.5% NaNO ₃ and 54.5% KNO ₃	0.0315	0.377	10.9
KCl	0.0125	0.128	10.3
KBr	0.0126	0.143	11.3
LiCl	0.0162	0.173	10.7

The numbers in the last column are remarkably close to each other, thus showing that for these substances the temperature coefficient of the viscosity of a salt is very nearly proportional to its viscosity.

The Viscosity of Metals.

Experiments were tried with copper, zinc, lead, tin, bismuth, cadmium, and mercury. It was found that the viscosity values were much lower than had been expected. Metals are, in fact, of the same order of viscosity as the salts just examined. Considerable difficulty has so far been experienced in obtaining trustworthy numbers for the

metals, and in the meantime the only figures given are such as could easily be repeated with the same result. These numbers were obtained from mercury, tin, lead, bismuth.

TABLE XVII.

Substance.	Temperature.	Density.	Viscosity.
Mercury	65°	13.43	0.0133
	95	13.39	0.0124
	133	13.27	0.0116
	216	13.08	0.0106
Tin (m. p. 232°).....	231	7.00	0.0275
	267	6.98	0.0235
	330	10.65	0.0320
Lead (m. p. 327°)	347	10.63	0.0293
	360	9.91	0.0167
Bismuth (m. p. 270°).....			

If these metals are compared at temperatures equally above their melting points, it is seen that lead is more viscous than tin, tin than bismuth, and bismuth than mercury. But they are closer to one another than would probably have been anticipated.

An important fact which has been noticed is that the viscosity of a metal does not increase in any abrupt manner as the temperature is lowered until it is actually solid. In many cases experiments were carried out with the metal in the crucible half solidified (round the sides), and no difference in viscosity could be detected between this temperature and a temperature a few degrees above this when all was fluid.

Conclusions.

1. The viscosity of many salts and metals is relatively small, being only a few times that of water.
2. The viscosities of sodium and potassium salts of the same acid are nearly the same.
3. Viscosity diminishes with rising temperature. The temperature coefficients for the salts examined vary directly as their viscosities.
4. A eutectic mixture at its melting point has a greater viscosity than the components have at their molting points.

I am much indebted to the Carnegie Trust for the Scottish Universities and to the Chemical Society for grants in aid of this research.

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CXXV.—*The Formation of Polyiodides in Nitrobenzene Solution. Part III. The Chemical Dissociation of the Polyiodides of the Alkali Metals and Ammonium Radicles.*

By HARRY MEDFORTH DAWSON.

IN a previous paper (Part I, Dawson and Gawler, *Trans.*, 1902, 81, 524) it has been shown that potassium iodide is readily soluble in nitrobenzene in presence of iodine. Solubility measurements indicated that dilute solutions, saturated with potassium iodide, contain one mol. of iodide per mol. of iodine, whereas solutions saturated with iodine contain four mols. of iodine per mol. of iodide. It is evident that the conditions obtaining in the two series of experiments—saturation with respect to iodide in the one case and with respect to iodine in the other—are such as might be expected to yield information relative to the lowest and highest types of polyiodides respectively, and the experimental data led the authors to conclude that the chief constituents of the two series of solutions are the tri-iodide and the enne-iodide.

Dawson and Goodson (Part II, *Trans.*, 1904, 85, 796) have shown that polyiodides of these types are also formed in nitrobenzene under the same conditions by the other alkali metals, the alkaline earth metals, and by ammonium and the substituted ammonium radicles. That polyiodides of the types MI_3 and MI_9 are also formed in certain other solvents has been shown to be probable (Dawson, *Trans.*, 1904, 85, 467), although, in general, the polyiodides are not so sharply defined in these solutions as they are when nitrobenzene is the solvent. Several factors contribute to this circumstance, so far as the experimental investigation of the polyiodides is concerned. In the first place, the polyiodides are, in general, readily soluble in nitrobenzene, whilst the simple iodides are, for the most part, only very sparingly soluble. To this statement certain substituted ammonium iodides represent exceptions. Then, again, iodine itself only dissolves to a comparatively small extent in nitrobenzene; the saturated solution at 18° contains approximately 0.2 mol. per litre. The very slight miscibility of nitrobenzene and water represents another factor of importance in connexion with the investigation of the soluble polyiodides, for this permits of a direct comparison of two different solutions of polyiodides which are in equilibrium with one another.

In the experiments described in this paper, an attempt has been made to ascertain the several types of polyiodides which are formed in

nitrobenzene solutions and the relationships which exist between the various types by a study of the distribution of iodine and iodides between nitrobenzene and water. The polyiodides of potassium have been examined more particularly, but comparative measurements have also been made in which the polyiodides of ammonium, substituted ammonium and the other alkali metals were submitted to investigation.

Jakowkin (*Zeitsch. physikal. Chem.*, 1894, 13, 539; 1896, 20, 19) has shown that the proportions of free and combined iodine in dilute aqueous solutions containing iodine and alkali or alkaline earth metal iodides are in agreement with the assumption of a dissociation equilibrium corresponding with the equation $MI_3 \rightleftharpoons MI + I_2$. If v is the volume of solution which contains one mol. of iodine as titrated by sodium thiosulphate solution, α the number of mols. of iodide contained in this volume, x the fraction of the iodine which is present in the free state, then the concentrations of the tri-iodide, iodide, and iodine are respectively $(1-x)/v$, $(\alpha-1+x)/v$, and x/v , and the equilibrium constant K is given by the equation:

$$K = \frac{x(\alpha-1+x)}{v(1-x)} \quad (1).$$

When the value of the constant K is known, and v and α for a given solution are determined by experiment, this equation may be used to calculate x/v , the concentration of the free iodine in the solution.

The possibility of obtaining the concentration of the free iodine in an aqueous iodine-iodide solution by this means has been utilised in the examination of nitrobenzene solutions of the polyiodides. When, for example, potassium iodide and iodine are shaken at constant temperature with excess of nitrobenzene and water until a condition of equilibrium is reached, two solutions containing polyiodides are obtained. The distribution of the iodine and potassium iodide between the two liquids is determined by definite partition coefficients characteristic of these substances, and by the formation of more or less stable polyiodides.

According to Jakowkin's investigations (*loc. cit.*), the nature of aqueous iodide-iodine solutions is very simple; provided the concentrations of the iodide and iodine do not exceed certain limits, the equilibrium can be represented by the equation $KI_3 \rightleftharpoons KI + I_2$. The concentration of the free iodine in any such solution can be determined from equation (1), and if the ratio of distribution of iodine between nitrobenzene and water is known, the concentration of the free iodine in the nitrobenzene solution, which is in equilibrium with this aqueous solution, may be deduced.

According to this method, the uncombined iodine in nitrobenzene

solutions containing iodine and potassium iodide in different proportions has been estimated. For the application of the method, measurements of the constant K at 18° and of the partition of iodine between nitrobenzene and water at different concentrations were required.

The constant K was determined by the method previously described (Dawson, Trans., 1901, 79, 238). Carbon tetrachloride was used in measuring the concentration of the free iodine in the aqueous solutions. The two following experiments give the value of the partition coefficient of iodine between carbon tetrachloride and water at $18^\circ \pm 0.02^\circ$. The concentrations are expressed in mols. per litre.

TABLE I.

Iodine concentration in CCl_4 .	Iodine concentration in H_2O .	Distribution ratio.
0.03438	0.0004153	82.7
0.04426	0.000535	82.8
		Mean 82.8

This value of the ratio was used in obtaining the free iodine concentration of the two aqueous iodide-iodine solutions examined, for which the experimental data and the calculated values of K are contained in table II.

TABLE II.

Aqueous solution.	Carbon tetrachloride solution.	K .
0.1 molar KI	0.02975 molar iodine	0.001153
0.02413 " iodine		
0.1 " KI	0.03083 " "	0.001153
0.02479 " iodine		

To ascertain the ratio of distribution of iodine between water and nitrobenzene, experiments at widely different concentrations were made. The quantities of the two liquids employed were largely increased as the iodine concentration was diminished, and in the case of the most dilute solutions 100 c.c. of nitrobenzene and 750 c.c. of water were used, the iodine concentration in the aqueous layer being obtained by titration of 500 c.c. with $N/100$ thiosulphate solution. The experimental data are contained in table III, the concentrations being expressed in mols. per litre.

TABLE III.

Iodine concentration in $\text{C}_6\text{H}_5\text{NO}_2$.	Iodine concentration in H_2O .	Distribution ratio.
0.03325	0.000191	174
0.03610	0.000207	174
0.0780	0.000451	173
0.0854	0.0004965	172
0.2275	0.001330	171
0.3328	0.001893	176

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The numbers in the third column indicate that the ratio of distribution of iodine between the two solvents is independent of the concentration, and the mean value is taken as 174. From this constancy, the conclusion may be drawn that the molecular complexity of iodine in the two solvents is the same.

Two experiments were also made to ascertain the ratio of distribution of potassium iodide between the two solvents. In consequence of the slight miscibility of the two liquids, this ratio differs in all probability very considerably from the ratio of the solubilities of the iodide in water and dry nitrobenzene. Both determinations were made on saturated solutions, a large volume of nitrobenzene and a small volume of water being shaken up with excess of potassium iodide; after remaining in the thermostat for about twenty-four hours, the concentration of the solutions was determined, the nitrobenzene solution being extracted for this purpose with successive small quantities of water, which was then evaporated to dryness. Table IV gives the experimental data, the concentrations being expressed in mols. per litre.

TABLE IV.

KI in water.	KI in nitrobenzene.	Distribution ratio.
6.05	0.00114	5300
6.05	0.00108	5600
		Mean 5450

The results obtained in these preliminary experiments have been utilised in the estimation of the free iodine in nitrobenzene solutions containing known quantities of potassium iodide and iodine. In order to illustrate the essential features of the experimental method, the mode of procedure which was tried in the first instance may be described. A definite quantity of water was shaken at 18° with successive quantities of a nitrobenzene solution (referred to as solution A) until the composition of the aqueous solution had become constant, and no change could be observed when it was agitated with a further quantity of solution A. The concentration of the iodine in the aqueous solution was then determined by titration, and that of the iodide by evaporation of a measured volume. By means of equation (1), the concentration of the free iodine in the aqueous solution is then obtained, and by multiplication of this value by the partition-coefficient of iodine distributing itself between nitrobenzene and water, the concentration of the free iodine in solution A is deduced.

Two or three preliminary experiments sufficed to show that this method of reaching the aqueous solution in equilibrium with solution A by a process of approximation could not be conveniently applied as a general method because of the large quantities of solution A required.

An alternative method, which consisted in shaking up solution *A* with aqueous potassium iodide solutions, the original concentrations of which were respectively greater and less than the concentration of the equilibrium solution, was found to be more convenient. The composition of the two aqueous solutions, after shaking with *A*, was determined, and from the changes in composition the composition of the equilibrium aqueous solution was deduced by interpolation. For an accurate measurement of the desired concentration by this method, the two aqueous solutions which are shaken up with solution *A* must not differ too greatly from the equilibrium solution the composition of which is sought. On account of the relatively small quantities of iodine which are removed when the solution *A* is shaken with the aqueous solutions, the addition of iodine to these solutions was not considered necessary; the iodine concentration of the equilibrium solution has therefore been simply determined by interpolation from the iodine concentrations of the two aqueous solutions used in the estimation of the equilibrium concentration of the iodide.

The actual data obtained in the determination of the aqueous solution which is in equilibrium with a nitrobenzene solution containing potassium iodide and iodine in quantities corresponding with the formula $0.1 \text{ molar (KI + 7I)}$ may be recorded as an illustration of the application of the method. Twenty-five c.c. of this solution were shaken with 50 c.c. of (1) 0.010 molar aqueous potassium iodide, (2) 0.015 molar aqueous potassium iodide. After shaking, the first aqueous solution was found to contain 0.0112 mol. of potassium iodide and 0.00334 mol. of iodine per litre, and the second solution 0.0140 mol. of potassium iodide and 0.00369 mol. of iodine per litre. The two original solutions are thus seen to contain respectively less and more potassium iodide than the equilibrium solution, and by interpolation this is found to contain 0.0125 mol. of potassium iodide per litre; the interpolated iodine concentration corresponding with this is 0.00351 mol. per litre.

In this way the composition of the aqueous solutions in equilibrium with 0.1 molar nitrobenzene solutions of potassium iodide, containing respectively 2, 3, 4, 5, 6, 7 and 8 atoms of iodine per mol. of iodide, has been determined. The data are collected in table V, concentrations being expressed in mols. per litre.

TABLE V.

	Composition of nitrobenzene solution.	Composition of aqueous solution.	
		Potassium iodide.	Iodine.
(1)	0.1 molar (KI + 2I)	6.05	0.00050
(2)	" (KI + 3I)	0.62	0.00435
(3)	" (KI + 4I)	0.22	0.00535
(4)	" (KI + 5I)	0.646	0.00480
(5)	" (KI + 6I)	0.022	0.00412
(6)	" (KI + 7I)	0.0125	0.00351
(7)	" (KI + 8I)	0.0073	0.00305
(8)	" KI saturated with iodine	0.0027	0.00226

In the first and last experiments the two solutions were in contact with undissolved potassium iodide and iodine respectively. On examination of the two series of numbers it is seen that the concentration of the iodide in the aqueous solution decreases rapidly as the relative proportion of iodine in the nitrobenzene solutions increases; the ratio of the iodide concentrations for the first and last solutions is approximately 2200:1. The iodine concentrations of the aqueous solutions are all very small compared with those of the corresponding nitrobenzene solutions; for the first solution, the ratio of these iodine concentrations is 1:200, although the concentration of the iodide in the aqueous solution is sixty times as large as it is in the nitrobenzene solution. These relationships indicate that nitrobenzene is a solvent which is most markedly favourable to the existence of the polyiodides which are the subject of this investigation.

A much clearer insight into the nature of the relationships, which exist between the corresponding aqueous and nitrobenzene solutions, is obtained when the concentrations of the free iodine are calculated in the manner already described. In table VI the first column gives the composition of the nitrobenzene solution; the second, the volume (v) in litres of the aqueous solution which contains 1 mol. of iodine titrated by thiosulphate solution; the third, the molar ratio (a) of iodide to iodine in the aqueous solution; the fourth, the fraction (x) of the total iodine present in the free state; the fifth, the concentration (x/v) of the free iodine in the aqueous solution; and the sixth, the concentration ($174x/v$) of free iodine in the nitrobenzene solution.

TABLE VI.

Composition of nitrobenzene solution.	v .	a .	x .	x/v .	$174 x/v$.
0.1 molar (KI + 2I)	2600	121.00	0.00019	0.000000095	0.0000165
" (KI + 3I)	230	142	0.00189	0.0000082	0.00143
" (KI + 4I)	187	41.1	0.00533	0.0000288	0.00504
" (KI + 5I)	208	9.53	0.0270	0.000130	0.0226
" (KI + 6I)	243	5.34	0.050	0.000247	0.0430
" (KI + 7I)	285	3.56	0.110	0.000386	0.067
" (KI + 8I)	323	2.40	0.193	0.00059	0.103
" KI saturated with iodine }	442	1.20	0.44	0.00100	0.174

The numbers in the last column are those to which attention must be directed. These have been calculated on the assumption that equation (1) expresses the relationship between free and combined iodine in the aqueous solutions which are in equilibrium with the various nitrobenzene solutions. With the exception of the first aqueous solution, all these are within the limits for which the validity of equation (1) may be said to have been established experimentally (compare Jakowkin, *loc. cit.*). For the solution saturated with iodine, the experiments of Noyes and Seidensticker (*Zeitsch. physikal. Chem.*, 1898, 27, 357) indicate that the quantities of free and combined iodine are in agreement with the requirements of the dissociation equation $KI_3 \rightleftharpoons KI + I_2$. It is therefore only in respect of the first solution, where the molar ratio of iodide to iodine reaches the very high value of 12100, that the validity of this equation may be said to lack experimental proof. That any polyiodide other than potassium tri-iodide is present in the saturated potassium iodide solution is, however, very improbable, and it may be confidently assumed that the concentration of the free iodine in this solution may also be obtained at least approximately by means of equation (1). In consequence of the high concentration of the iodide in the aqueous solution, the distribution of the free iodine between the two liquids will no doubt in this case undergo an alteration which is considerably greater than that resulting from the "salting out" action in the case of the other solutions, and to this extent the calculated concentration of free iodine in the first nitrobenzene solution is somewhat doubtful.

Comparing the numbers in the last column of the preceding table, it is evident that the free iodine concentration increases enormously as the molar ratio of iodine to iodide increases from one to four; the ratio of the values for the solutions KI_3 and KI_4 is 6200:1. In the interpretation of these numbers it may be recalled that the existence of the polyiodides KI_3 and KI_4 has been established as the result of solubility measurements, and that these represent the lowest and highest polyiodides which are capable of existence in nitrobenzene solutions. As yet, however, no evidence of the existence of definite intermediate types has been brought forward. From the fact that all the polyhalogen compounds of the alkali metals which have been prepared as crystalline substances are of the types MX_3 or MX_4 (compare Wells, *Zeitsch. anorg. Chem.*, 1892, 1, 85; Wells and Wheeler, *ibid.*, 1892, 1, 442; 1892, 2, 255), that the polyiodides of the alkali metals, the existence of which, in the free state, is indicated by the iodine tension measurements of Abegg and Hamburger (*Zeitsch. anorg. Chem.*, 1906, 50, 403), are of the types MI_3 , MI_4 , MI_5 , or MI_6 , and that the crystallised polyiodides of the substituted ammonium bases are of these same types, it might be expected that the intermediate poly-

iodides KI_5 and KI_7 are contained in nitrobenzene solutions the composition of which corresponds with these formulæ. On the other hand, it is possible that such solutions represent mixtures of the highest and lowest polyiodides in accordance with the equations (a) $3KI_5 = 2KI_3 + KI_9$, and (b) $3KI_7 = KI_3 + 2KI_9$.

It appears possible to decide which of the two views corresponds with fact by the following consideration. If the 0.1 molar solution of the composition $(KI + 4I)$ represents a mixture of the tri- and ennea-iodide in accordance with equation (a), the concentration of the ennea-iodide in the solution should be 0.033 molar. Measurement of the free iodine concentration in a 0.033 molar KI_9 solution gave 0.0405 mol. per litre, while according to the previous table a 0.1 molar solution of the composition $(KI + 4I)$ contains 0.00504 mol. free iodine per litre. These numbers are as 8 to 1, and the very large difference between the free iodine concentrations of these two solutions must be interpreted as in favour of the view that a nitrobenzene solution of the composition $(KI + 4I)$ contains a definite polyiodide KI_5 as the chief component. By similar reasoning it is possible to show that the polyiodide KI_7 is present in nitrobenzene solutions which contain more iodine.

The conclusion that four polyiodides, KI_3 , KI_5 , KI_7 and KI_9 , are formed in nitrobenzene solution agrees very satisfactorily with the numbers which express the free iodine concentrations of the nitrobenzene solutions (1) to (8) in table VI if we assume that chemical dissociation of the polyiodides takes place in accordance with the scheme: $KI_9 \rightleftharpoons KI_7 + I_2$; $KI_7 \rightleftharpoons KI_5 + I_2$; $KI_5 \rightleftharpoons KI_3 + I_2$; $KI_3 \rightleftharpoons KI + I_2$. Although it is not possible to subject the four stages in the dissociation process to a separate minute analysis, a comparison of the percentage amounts of free iodine in 0.1 molar solutions of the composition KI_3 , KI_5 , KI_7 and KI_9 respectively gives some idea of the extent of the dissociation in the several stages. The numbers in table VII represent the percentage amounts of free iodine in terms of the total iodine as titrated by thiosulphate solution.

Table VII.

Composition of solution.	KI_3 .	KI_5 .	KI_7 .	KI_9 .	Saturated with iodine.
Percentage iodine dissociation	0.016	2.5	14	26	32

From these numbers it is evident that the dissociation of the tri-iodide is extremely small, whereas that of the ennea-iodide is very considerable; the value 26 can only be interpreted on the assumption that dissociation in the ennea-iodide solution has taken place, not only in accordance with the first equation, but also to an appreciable extent according to the second. In reference to the solution saturated

with iodine, it may be noted that this contains 5.50 mols. of iodine per mol. of iodide. Of this, 32 and 68 per cent. respectively are present in the free and combined states; the ratio of combined iodine to iodide is therefore expressed by the formula $KI_{3.3}$, from which it is evident that the dissociation of the enne-iodide is very considerably diminished in presence of the excess of iodine corresponding with the saturated solution.

Influence of the Concentration of the Solution on the Dissociation of KI_9 .—With the object of obtaining further information in regard to the dissociation of the polyiodides, the amount of free iodine in enne-iodide solutions of different concentrations has been examined. In these experiments, 0.01, 0.033, 0.1 and 0.48 molar solutions of the composition KI_9 were shaken at 18° with aqueous iodide solutions of known concentration, and from the changes undergone by the aqueous solutions the composition of the aqueous solution which is in equilibrium with each of the four nitrobenzene solutions was deduced. The concentration of the free iodine in these was then calculated as previously described. Table VIII contains the results of this investigation, the several columns of figures having the signification given previously in connexion with table VI.

Table VIII.

Concentration of KI_9 solution.	r .	a .	x .	x/a .	174 x/r .	Dissociation per cent.
0.48 molar	105.3	2.00	0.100	0.000950	0.165	8.6
0.10 "	328	2.40	0.193	0.000590	0.103	25
0.033 "	617	5.06	0.144	0.000233	0.0405	30
0.01 "	1600	12.8	0.131	0.0000838	0.0146	36

The iodine dissociation evidently increases with the dilution of the solution, and the observed variation leads to the conclusion that in more concentrated solutions, such as were examined by means of solubility measurements, the enne-iodide is dissociated to a comparatively small extent. The calculated value of the dissociation is based on the assumption that the iodine distribution is determined in all cases by the ratio 174; the uncertainty hereby involved increases with the concentration, and on this account more concentrated solutions were not submitted to examination.

Dissociation of different Ennea-iodides.—The experiments of which an account has so far been given refer solely to potassium iodide solutions. If polyiodide solutions of the other alkali metals were subjected to a minute examination, similar relationships would no doubt be found. To ascertain whether quantitative differences in the degree of chemical dissociation are exhibited, solutions containing lithium, sodium, potassium, rubidium, cesium, ammonium and tetramethyl-ammonium iodide have been compared. To effect this comparison in

a complete manner would have involved the determination of the composition of the aqueous solutions which are in equilibrium with the tri-, penta-, hepta-, and ennea-iodide solutions of each of the alkali metals and ammonium bases. The fact that the accurate measurement of the free iodine in the tri-iodide solutions necessitates the use of large quantities of materials, and that the validity of equation (1) for the concentrated aqueous solutions has not been experimentally demonstrated, has limited the inquiry in the case of the tri-iodides to sodium and potassium. For the rest, it was considered sufficient to compare the ennea-iodide solutions, and this comparison has been made for 0.1 molar solutions without determining exactly the composition of the aqueous solutions with which the nitrobenzene solutions are in equilibrium.

In this comparative investigation, 50 c.c. of each of the ennea-iodide solutions were shaken with an equal volume of water, and the concentration of iodide and iodine in the aqueous solution determined.

In table IX, the iodide under investigation is indicated in the first column, the second and third columns give the concentration of the iodide and iodine in the aqueous solutions, the fourth gives the calculated concentration of free iodine in the nitrobenzene solutions, and the fifth the percentage iodine dissociation.

TABLE IX.

Iodide.	Aqueous solution.		Nitrobenzene solution.	
	Iodide.	Iodine.	Free iodine.	Dissociation per cent.
$N(CH_3)_4I_9$	0.00015	0.00075	0.104	26
CsI_9	0.00117	0.00105	0.110	27
RbI_9	0.00387	0.00189	0.102	25
KI_9	0.00665	0.00281	0.101	25
NH_4I_9	0.0120	0.00471	0.104	26
NaI_9	0.0308	0.0135	—	—
LiI_9	0.0456	0.0225	—	—

In this table the iodides are arranged in the order of increasing concentration of the aqueous solution. From the numbers in the second and third columns, it is evident that the quantities of the iodides and of iodine which are removed by water from the several ennea-iodide solutions vary very considerably; the particular iodide in a given ennea-iodide solution can indeed be at once recognised by the intensity of the colour of the aqueous extract. In consequence of the removal of iodide by the water, the composition of the nitrobenzene solution changes to an extent which depends on the particular iodide present. This change is negligible in the case of tetramethyl-ammonium, small for caesium and rubidium, considerable for potassium and ammonium, and very large for sodium and lithium. Although in

consequence of this circumstance the data obtained for the various solutions are not all comparable, it appears at first sight as if the dissociation depends very largely on the metal (or radicle) contained in the ennea-iodide solution. If, however, the concentration of the free iodine in the various nitrobenzene solutions is calculated from the composition of the corresponding aqueous solutions, a very nearly constant value is obtained, as is evident from the numbers in the fourth and fifth columns of the table. That the values of the free iodine concentration and the dissociation calculated in this way are approximately the same as those which would be obtained from the aqueous solutions in equilibrium with the accurately 0.1 molar ennea-iodide solutions is shown by the close agreement of the values in the case of potassium; these are respectively 25 and 26 per cent. for the iodine dissociation.

It should be noted that the aqueous solution obtained by extraction of the tetraethylammonium ennea-iodide solution with water contains more iodine than iodide, and in the calculation it has been assumed that all the iodide is present in the form of tri-iodide. The same constant, $K = 0.001155$, has been used as determining the equilibrium in the aqueous solution for all the iodides examined. Jakowkin's experiments (*loc. cit.*) indicate that this is justified for sodium and lithium solutions, and a determination for a caesium iodide solution gave the same value for the constant as has been found in the case of potassium iodide.

On account of the large quantities of iodide and iodine which are extracted when the ennea-iodide solutions of sodium and lithium are shaken up with an equal volume of water, the data for these solutions in table IX cannot be utilised for the calculation which has been made in the case of the other five solutions. For the sodium ennea-iodide solution, the composition of the aqueous solution in equilibrium with it has, however, been determined by the method previously described; this solution was found to contain 0.080 mol. sodium iodide and 0.0248 mol. iodine per litre, and the proportion of free iodine in the ennea-iodide solution which is calculated from these numbers is 22 per cent., which agrees fairly well with the dissociation found in the case of the other iodides.

The above comparative measurements lead to the conclusion that the ennea-iodides of the alkali metals and ammonium bases are chemically dissociated to the same extent. It is evident that this may be explained if we assume that the free iodine is a dissociation product of iodine ions in accordance with the scheme: $I_9' \rightleftharpoons I_7' + I_2$; $I_7' \rightleftharpoons I_5' + I_2$; $I_5' \rightleftharpoons I_3' + I_2$; $I_3' \rightleftharpoons I' + I_2$. In support of this view, measurements of various physical properties of the polyiodide solutions will be communicated in a further paper.

As previously mentioned, a comparison of the quantities of iodine in the aqueous solutions obtained by shaking together a 0.1 molar nitrobenzene solution of iodine with water and excess of potassium or sodium iodide has been made. In the case of potassium, the aqueous solution was found to contain 6.05 mols. of iodide and 0.00050 mol. of iodine per litre, while the sodium solution contained 8.11 mols. of iodide and 0.0011 mol. of iodine per litre. The free iodine in the two nitrobenzene solutions corresponding with these data is about 0.02 per cent.; the chemical dissociation of both the tri-iodides is therefore very small. The very unequal distribution of the iodine in these circumstances, coupled with the fact that the tri-iodides are so readily soluble in water, leads to the supposition that the tri-iodides in the nitrobenzene solution are combined in some way with the solvent. The fact that water removes widely different quantities of iodides and iodine from enne-iodide solutions of the various alkali metals and ammonium bases can also be accounted for on this hypothesis if the compounds formed by the polyiodides with the nitrobenzene are of different degrees of stability.

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CXXVI.—*The Study of the Absorption Spectra of the Hydrocarbons isolated from the Products of the Action of Aluminium Chloride on Naphthalene.*

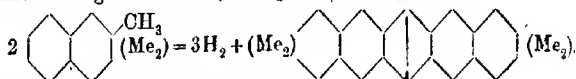
By ANNIE HOMER, Fellow of Newnham College, and
JOHN EDWARD PURVIS, M.A.

From the products of the action of aluminium chloride on naphthalene, besides $\beta\beta$ -dinaphthyl previously isolated by Friedel and Crafts from the same reaction, there have been isolated three new hydrocarbons which have been described in detail by one of us (Homer, Trans., 1907, 91, 1103). The substances isolated were:

- (i) $C_{14}H_{16}$, a homologue of naphthalene, either tetramethyl- or
4 s 2

diethyl-naphthalene, more probably the former; (ii) $C_{26}H_{16}$, $\beta\beta$ -dinaphthyl; (iii) $C_{26}H_{22}$, a substance supposed to be a homologue of dinaphthanthracene, $C_{22}H_{14}$; and (iv) $C_{40}H_{26}$, probably tetra-naphthyl.

$\beta\beta$ -Dinaphthyl is formed by the condensation of two naphthalene molecules. It was thought that the hydrocarbon $C_{40}H_{26}$ was formed by the condensation of either two $\beta\beta$ -dinaphthyl or four naphthalene molecules, more probably by the former, as an increase in the time allowed for the action of aluminium chloride on naphthalene, or a rise in the temperature at which the reaction was conducted, caused a decrease in the amount of the hydrocarbon $C_{26}H_{14}$ and an increase in the amount of the hydrocarbon $C_{40}H_{26}$ produced. It was suggested that the substance $C_{26}H_{22}$ was a homologue of dinaphthanthracene, $C_{22}H_{14}$, and its formation from alkyl-naphthalenes, which are also formed during the reaction, was given as follows:



The intense fluorescence of the substance suggested the presence of an anthracenoid linking.

In the method of formation thus proposed, hydrogen would be eliminated from a β -methyl group of trimethylnaphthalene. It was thought (*loc. cit.*) that further evidence as to the constitution of the respective products of the reaction in question might be produced from a comparative study of their absorption spectra with that of naphthalene; and it was also suggested that the absorption spectrum of the hydrocarbon $C_{26}H_{22}$ should be compared with that of the supposed parent substance, dinaphthanthracene, $C_{22}H_{14}$, and of picene, the isomeride of dinaphthanthracene.

It was with these objects in view that the investigation here described was undertaken.

EXPERIMENTAL.

The hydrocarbons $C_{14}H_{10}$, $C_{20}H_{14}$, $C_{40}H_{26}$, $C_{26}H_{22}$, were prepared according to the methods given in the paper by Homer (*loc. cit.*).

The standard strength of our solutions was taken as $N/1000$, a normal solution being considered as a solution containing one gram-molecular weight of solute in 1000 c.c. of the solution.

The adjustable cell used has been previously used and described by Purvis and Foster (*Proc. Camb. Phil. Soc.*, 1907, 14, 381). It is a modification of the very useful instrument described by Baly and Desch (*Trans.*, 1904, 85, 1029).

The results of the study of the absorption spectra of the substances under consideration have been plotted in the accompanying curves so

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that the abscissae represent oscillation frequencies, and the ordinates the logarithms of relative thicknesses of the solution. From eye observations we could observe directly the bands due to the hydrocarbon $C_{26}H_{42}$, and the absence of bands in the hydrocarbons $C_{40}H_{68}$, $C_{20}H_{34}$, $C_{14}H_{22}$; but in order to compare the absorption curves with those of other substances like naphthalene we decided to plot the curves in exactly the same way, so as to obtain comparable results.

I. *Naphthalene and $C_{14}H_{10}$.*

The absorption spectrum of naphthalene has been given in detail by Hartley (Trans., 1881, 39, 153), who has shown that there are four bands characteristic of this substance. Their mean wave-lengths are:

2855	2726	2631	2550
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which correspond with oscillation frequencies of:

3451	3690	3840	3921
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The curve for an $N/1000$ solution of the hydrocarbon $C_{14}H_{10}$ in alcohol also shows four bands (Fig. 1). The mean oscillation frequencies of these bands are as follow:

3434	3562	3680	3776
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These four bands are thus nearer the red end of the spectrum and appear to be less persistent than the corresponding bands in the naphthalene curve. The curve for the hydrocarbon $C_{14}H_{10}$ is therefore in accordance with the suggestion in the previous paper that this substance is an alkyl derivative of naphthalene. It is suggested on p. 1327 that the methyl groups are probably in the 1, 4, 5, 8 positions.

II. *The Hydrocarbons $C_{20}H_{34}$ and $C_{40}H_{68}$.*

$N/10,000$ solutions of these compounds in benzene were compared. It was found that stronger solutions did not show selective absorption. The curves for both these substances in benzene show only two weak bands (Fig. 2). The mean oscillation frequencies of these bands were:

For $C_{20}H_{34}$	3184	3430
For $C_{40}H_{68}$	3060	3200

The bands exhibited by the solutions of the hydrocarbon $C_{40}H_{68}$ are nearer the red end of the spectrum than those exhibited by solutions of the hydrocarbon $C_{20}H_{34}$; but in the former case they are so weak that they may be regarded as traces.

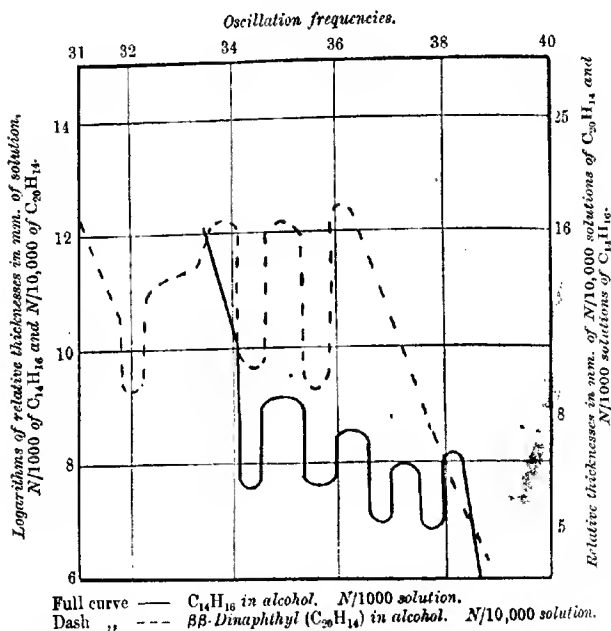
Since benzene solutions of the hydrocarbons $C_{20}H_{34}$ and $C_{40}H_{68}$ exhibit the same type of curve, it seems reasonable to infer that these

substances have a similar constitution. The hydrocarbon $C_{20}H_{14}$ has been shown to be $\beta\beta$ -dinaphthyl by Watson Smith (Trans., 1877, 15, 551; 1879, 17, 224) and Chattaway (Trans., 1895, 67, 653).

The hydrocarbon $C_{40}H_{26}$ therefore probably has the constitution which has already been suggested, namely, that of tetranaphthyl. At the present stage it is impossible to state how the two $\beta\beta$ -dinaphthyl molecules have been condensed to yield tetranaphthyl.

In order to compare the absorption spectrum of $\beta\beta$ -dinaphthyl with that of naphthalene, it was necessary to examine it in alcoholic

FIG. 1.



solution. An $N/10,000$ solution of $\beta\beta$ -dinaphthyl in alcohol (Fig. 1) shows three absorption bands of which the mean oscillation frequencies are:

3204

3436

3556

It is remarkable that whilst naphthalene in alcoholic solution gives four bands, $\beta\beta$ -dinaphthyl in the same solvent gives only three bands, although $\beta\beta$ -dinaphthyl consists of two naphthyl groups.

Now there are two possible explanations of this phenomenon, which are as follows:

(i) *The diminished absorption power is due to steric hindrance.* The molecule of $\beta\beta$ -dinaphthyl may be so arranged in space that there is crowding within the molecule such that the vibrations of some of the carbon atoms within one naphthyl group are hindered by the too close proximity of vibrating atoms in the other naphthyl group. The effect of this hindrance will be evidenced by a decrease either in the rate or the amplitude of the vibrations of the atoms affected. In either case the effect of the steric hindrance will be evidenced by a diminished capacity for selectively absorbing light, although the increased size of the molecule will increase the general absorption.

(ii) *The diminished absorption power may be due to the twisting of one naphthyl group relatively to the other.* If there is twisting in one of the naphthyl groups, the atoms in that group will no longer vibrate in the same plane as the corresponding atoms in the other group. The twisting effect is probably more marked for some of the atoms than for the others. Consider the effect of this twisting in the two extreme cases, where:

(a) The atoms are practically not affected. In this case the effect of the vibrations of these atoms on a ray of light will be the same as that of the corresponding atoms in the other naphthyl group. That is to say, the corresponding atoms of the two naphthyl groups will augment each other's absorbing power.

(b) The atoms are so much twisted that they vibrate in the same plane as the corresponding atoms in the other naphthyl group, but they are now in opposite phase. In this case the vibrating atoms nullify each other's effect on the ray of light. That is to say, if these atoms in the naphthalene molecule selectively absorbed light, they will now allow light to pass.

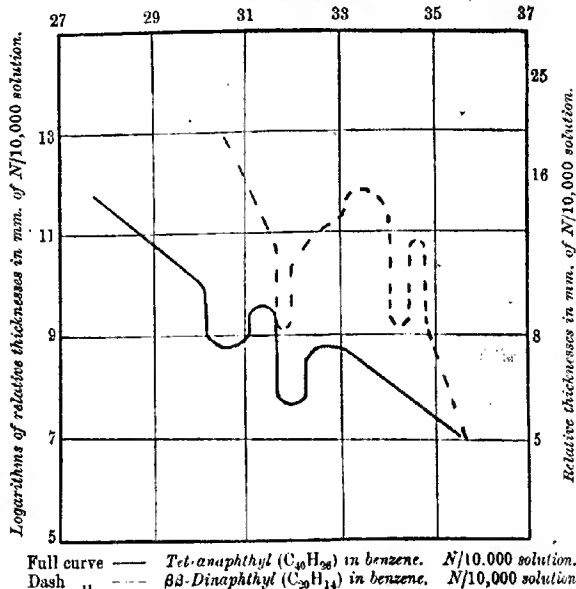
Moreover, between these two extremes cases there will be intermediate stages. But the total resultant effect of the various degrees of twisting of the second naphthyl group will be such that the selective absorption power of $\beta\beta$ -dinaphthyl is less than that of naphthalene.

If the above argument holds good, the decrease in selective absorption ought to be more marked in the case of tetranaphthyl. Owing to the insolubility of this hydrocarbon in alcohol it cannot be compared with naphthalene, but a glance at the curves in Fig. 2 shows that the two bands exhibited by this substance in benzene solution are so much weaker than the corresponding bands for $\beta\beta$ -dinaphthyl that they are practically eliminated. This fact is in accordance with the explanation offered above.

The effect of the increase in size of the molecule is shown by the fact that the alcoholic solution of $\beta\beta$ -dinaphthyl requires smaller

concentration for complete absorption than that of naphthalene. At the same time there is a shift in the position of the bands towards the red end of the spectrum. The same effects are shown by benzene solutions of tetranaphthyl and $\beta\beta$ -dinaphthyl. In the case of $\beta\beta$ -dinaphthyl, besides damping the third band, the benzene has

FIG. 2.
Oscillation frequencies.



slightly shifted the positions of the two remaining bands towards the red end of the spectrum.

III. Examination of Benzene Solutions of the Isomerides Picene and Dinaphthanthracene and of the Substance $C_{18}H_{22}$.

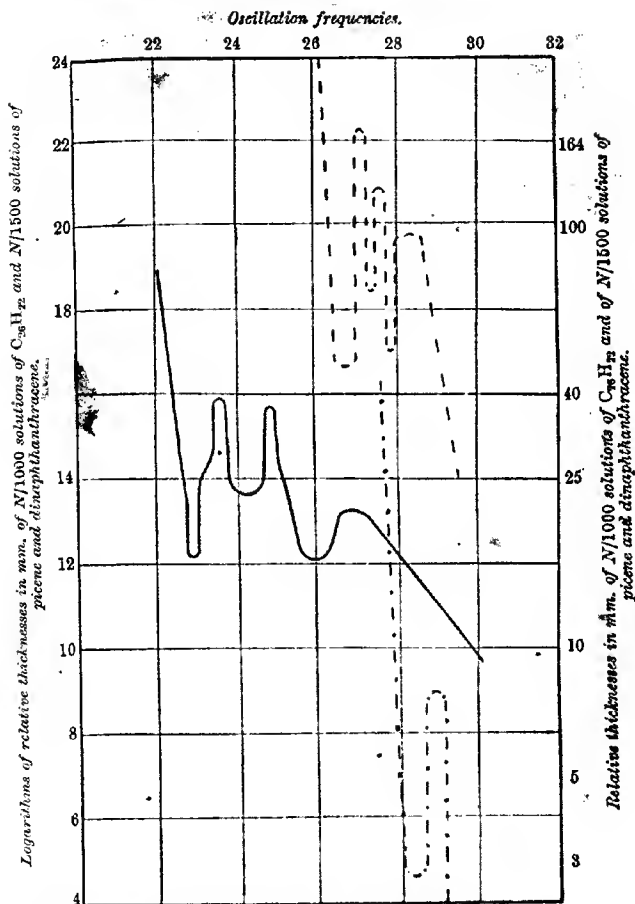
The strongest solutions of picene and dinaphthanthracene which could be prepared were $N/1500$. In the case of the hydrocarbon $C_{26}H_{22}$ which is very soluble in benzene, it was found more convenient to use an $N/1000$ solution. The difference between the strengths of the solutions of the hydrocarbon $C_{26}H_{22}$ and of the isomerides did not affect the conclusions to be drawn from the resulting curves.

ABSORPTION SPECTRA OF HYDROCARBONS.

1325

A comparative study of the curves shows that picene, as would be expected from Hartley's theory, exhibits a type of curve markedly

FIG. 3.



Full curve — N/1000 solution of $C_{26}H_{22}$ in benzene.

Dash --- N/1500 solution of picene in benzene.

Dot and dash curve - - - N/1500 solution of dinaphthanthracene in benzene.

different from that of dinaphthanthracene (Fig. 3). The curve for picene (Fig. 3) shows three well-marked bands of which the mean oscillation frequencies are:

2670

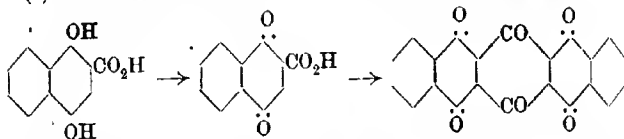
2732

2784

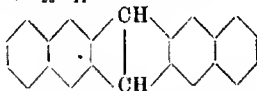
The first of these bands is the most persistent. A solution of dinaphthanthracene of the same strength (Fig. 3) shows only one band, the mean oscillation frequency of which is 2840. The persistency of this band is not quite so marked as that of the first picene band. Besides the fact that picene has three bands, it is also remarkable that these bands are all much nearer the red end of the spectrum than the band of dinaphthanthracene. It seems therefore as though in picene the vibrations of the carbon atoms within the molecule have a greater amplitude than in the molecule of the isomeric dinaphthanthracene. Picene has been shown to have a phenanthrene structure by Bamberger and Chattaway (*Ber.*, 1893, 26, 1751). Hartenstein (*Diss.*, Jena, 1892) has shown that dinaphthanthracene, from its method of formation, its properties, and the properties of its quinone, has a constitution similar to that of anthracene. Dinaphthanthracene was prepared by Hartenstein as follows:

Disodium or dipotassium α -naphthaquinol was heated with carbon dioxide under pressure and from the products of the reaction, by suitable treatment, α -naphthaquinol-2-carboxylic acid was isolated. The acid thus obtained was treated with concentrated sulphuric acid at 70°, whereby two reactions took place:

- (1) The acid was oxidised to α -naphthaquinonecarboxylic acid.
- (2) The oxidation product condensed to form a substance $C_{22}H_8O_6$.



This condensation product by distillation with zinc dust was reduced to dinaphthanthracene, $C_{22}H_{14}$:



A small amount of dinaphthanthracene was also prepared by the same method by Russig (*J. pr. Chem.*, 1900, [ii], 62, 30).

A study of the curve for the hydrocarbon, $C_{26}H_{22}$ (Fig. 3), shows that this substance has a constitution similar to that of picene and not of dinaphthanthracene, as had been previously supposed. The curve for $N/1000$ solutions of the hydrocarbon $C_{26}H_{22}$ in benzene shows three bands, of which the first is most persistent, with mean oscillation frequencies:

2290

2424

2584

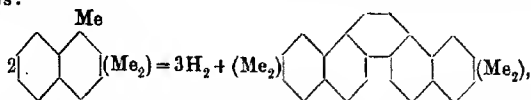
The bands are much nearer the red end of the spectrum than those

ABSORPTION SPECTRA OF HYDROCARBONS.

1327

in the picene curve. These facts are in accordance with previous observations that the introduction of groups into the nucleus causes a shift in position towards the red end, but in this case the shift has been so great that the bands are in the visible portion of the spectrum.

The formation of the hydrocarbon $C_{26}H_{22}$ probably takes place as follows:



thus entailing the elimination of hydrogen from methyl groups in the α -position. Now from the facts known of the action of aluminium chloride on benzene and its homologues it seems justifiable to infer that in the corresponding reaction with naphthalene the monoalkylated naphthalene first formed would be converted into di-, tri-, and tetra-alkylated naphthalenes. Moreover, as there is no apparent reason against the supposition that symmetrical products would be formed, the obvious inference is that since in the trimethylnaphthalene, the forerunner of the hydrocarbon $C_{26}H_{22}$, there is one methyl group in the α -position, then the others are also in α -positions, and therefore in the hydrocarbon $C_{26}H_{22}$ the methyl groups are also in α -positions.

Applying the same method of reasoning with regard to the position of the methyl groups, the hydrocarbon $C_{14}H_{10}$ will probably be 1:4:5:8-tetramethylnaphthalene.

Summary.

The results of the comparative study of the absorption spectra of the substances under consideration indicate:

I. That the substance $C_{14}H_{10}$ is a naphthalene derivative, probably 1:4:5:8-tetramethylnaphthalene.

II. That the hydrocarbon $C_{40}H_{26}$ has a constitution similar to that of $\beta\beta$ -dinaphthyl, and is therefore probably tetranaphthyl.

III. That picene and dinaphthantracene have markedly different absorption spectra.

IV. That the hydrocarbon $C_{26}H_{22}$ exhibits the same type of absorption curve as picene, and is therefore an alkyl derivative of picene.

There is still required some explanation of the intense fluorescence of the hydrocarbons $C_{40}H_{26}$ and $C_{26}H_{22}$. The investigation of these phenomena is a subject for future research.

The authors take this opportunity of thanking Prof. E. von Meyer for providing the sample of dinaphthantracene from Dr. Hartenstein's

specimen at Dresden, and also from Hammerger and Mr. Chittaway for so kindly sending specimens of picene, without which the work embodied in this paper could not have been so satisfactorily concluded.

The authors also desire to express their thanks to the Research Fund Committee of the Chemical Society for a grant which has in part defrayed the expenses of this investigation.

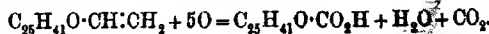
THE UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.

CXXXVII.—Cholestenone.

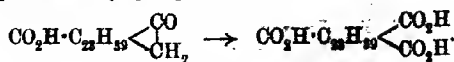
By CHARLES DORÉE and JOHN ADDYMAN GARDNER.

CHOLESTEROL, which is an unsaturated secondary alcohol of the formula $C_{27}H_{46}O$, may be oxidised, under suitable conditions, to an unsaturated ketone, cholestenone, $C_{27}H_{44}O$ (Diels and Abderhalden, *Ber.*, 1904, 37, 3092; Windaus, *Ber.*, 1906, 39, 518). Although the $CH-OH$ group of the cholesterol is converted to a carbonyl group in cholestenone, the behaviour of the two substances under the influence of reducing agents (*Ber.*, 1906, 39, 884; 1908, 41, 260) makes it doubtful whether their "carbon-skeleton" is identical in each case. In 1906 Windaus (*Ber.*, 39, 2008) studied the oxidation of cholestenone, using neutral permanganate which, according to Tiemann and Semmler (*Ber.*, 1895, 28, 1345), is less likely than other oxidising agents to produce intramolecular change. He obtained as the chief product a saturated keto-monocarboxylic acid, $C_{26}H_{42}O_3$, which contained one carbon atom less in the molecule than the parent substance, and which, on further oxidation, passed into a tricarboxylic acid, $C_{26}H_{42}O_6$.

These changes were, according to Windaus (*loc. cit.*), most simply explained by assuming that cholestenone contains a group, $CH:CH_2$, which is situated at the end of an open side-chain, so that the production of the acid may be represented by the following equation:



The tricarboxylic acid would then result by the rupture of the ring containing the carbonyl group thus:

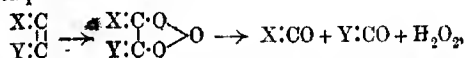


The correctness of this explanation is based on the analyses of the

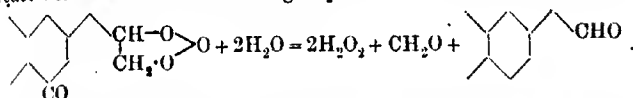
ketonic acid and its derivatives, and their recognition as C_{26} compounds, a point which is somewhat difficult to settle by combustion alone; for example, Windaus found for the keto-carboxylic acid the figures $C = 77.18$, 77.75 , $H = 11.14$, 11.18 . These values agree equally well with the formula $C_{26}H_{44}O_3$, which requires $C = 77.55$, $H = 10.52$, and with $C_{25}H_{40}O_3$, which requires $C = 77.26$ and $H = 10.38$ per cent.

When the analyses of all the derivatives prepared are considered together, the C_{26} carbon content appears the more preferable, but as the modern view of the formula of cholesterol and the interpretation given to the many derivatives obtained from it by oxidation is based on the work referred to, it seemed to us desirable to submit the question to a further test.

Harries has shown (*Annalen*, 1906, 343, 311) that unsaturated alcohols, when submitted to the action of ozone, combine with one molecule of ozone to form ozonides, whilst unsaturated ketones absorb four atoms of oxygen, namely, three at the ethylene linking and one at the carbonyl group. These ozonides on treatment with water decompose as follows:



aldehydes or ketones and hydrogen peroxide being formed. If Windaus's formula is correct, cholestenone should absorb four atoms of oxygen under the influence of ozone, and the ozonide formed should react with water in the following way:



These aldehydes would be at once oxidised by the hydrogen peroxide, and we should expect to find among the final products a C_{25} acid and probably either formic or carbonic acid derived from the form-aldehyde.

The action takes place broadly on the lines predicted, and we obtained as chief products the C_{26} ketonic acid described by Windaus, and carbon dioxide. Cholesterol, on similar treatment, formed an ozonide which also gave carbon dioxide on decomposition.

EXPERIMENTAL.

Ozonide of Cholestenone.—Ten grams of cholestenone were dissolved in 200 c.c. of dry chloroform, and a slow current of ozonised oxygen was bubbled through the solution until the ozone ceased to be absorbed and escaped freely. The chloroform was allowed to evaporate spontaneously, and the viscid oil left behind was dissolved in the

least quantity of ethyl acetate and poured into a large excess of light petroleum. A considerable proportion of the ozonide separated in a soft, resinous form, which was again dissolved and reprecipitated. The substance was placed in a vacuum desiccator and finally obtained as a colourless, glassy solid which was readily powdered. Two different preparations on analysis gave the following figures:

- I. 0.1767 gave 0.4224 CO_2 and 0.1458 H_2O . $\text{C} = 65.29$; $\text{H} = 9.17$.
 II. 0.1781 „ 0.4424 CO_2 „ 0.1459 H_2O . $\text{C} = 67.75$; $\text{H} = 9.10$.
 $\text{C}_{27}\text{H}_{44}\text{O}_6$ requires $\text{C} = 67.50$; $\text{H} = 9.17$.
 $\text{C}_{27}\text{H}_{44}\text{O}_7$ „ $\text{C} = 65.40$; $\text{H} = 8.87$ per cent.

These results seem to show that six or seven oxygen atoms are absorbed by the cholestenone molecule. We should have expected four atoms to be added in the case of a singly unsaturated ketone. It may be, however, that cholestenone contains a second ethylene linking which is not rendered apparent by the usual reagents.

Decomposition of the Ozonide by Water.—It was not, for subsequent experiments, found necessary to prepare the pure ozonide as above. Instead, the chloroform solution of the ozonide was mixed with about twenty times its volume of water and heated on the water-bath in a current of purified oxygen. The gases evolved were passed through measured quantities of standard baryta solution. The action was slow, the evolution of carbon dioxide continuing for many hours. The aqueous liquid remaining in the flask was milky, acid to litmus, and had a peculiar odour of orange oil which we have previously noticed in the course of some experiments on the oxidation of cholesterol with hydrogen peroxide. The solid product was left as a brown oil, which, on cooling, solidified to a brittle mass. This was dissolved in ether and the ethereal solution shaken with sodium carbonate to separate the acid products from unchanged cholestenone or other neutral substances.

The alkaline liquors were acidified when the acids separated in a thick clot. This, after drying, was extracted with light petroleum, which removed some oily, non-crystalline material and left the main product of the reaction in the form of a white powder, the yield being 25 per cent. of the original cholestenone. It was purified by recrystallisation from acetone and from a mixture of light petroleum and benzene, and was obtained from the latter solvent in leaves which melted at 155° :

- 0.2179 gave 0.6154 CO_2 and 0.2082 H_2O . $\text{C} = 77.02$; $\text{H} = 10.62$.
 $\text{C}_{26}\text{H}_{42}\text{O}_3$ requires $\text{C} = 77.55$; $\text{H} = 10.52$ per cent.

The quantity of carbon dioxide evolved in these experiments was always very much less than would correspond with the oxidation of a terminal CH_2 group to carbon dioxide. Thus 0.6745 of pure ozonide

gave 0.00649 of carbon dioxide, or about 1 per cent., whilst theory requires 9.8 per cent. In other experiments also the quantity obtained was about one-tenth part of that theoretically required. It seemed likely that this was due to the preferential oxidation of the C_{26} aldehydic substance, presumably formed, by the hydrogen peroxide. To test this we decomposed the crude product obtained by ozonising 10 grams of cholestenone, in the presence of very dilute hydrogen peroxide and sulphuric acid. The yield of carbon dioxide now obtained agreed very well with the explanation above suggested.

0.268 Gram of carbon dioxide was obtained together with 2.30 grams of the acid $C_{26}H_{42}O_3$. The quantity of carbon dioxide theoretically produced with this quantity of acid is 0.245 gram. The neutral products of the reaction contained a considerable quantity of unchanged cholestenone.

Identification of the Acid $C_{26}H_{42}O_3$.—The acid obtained by us agrees in all its properties with that obtained by Windaus by the oxidation of cholestenone with permanganate. On titration:

0.2571 required 6.37 c.c. $N/10$ sodium hydroxide. Equivalent = 403.
 $C_{26}H_{42}O_3$, monobasic, requires 402.

The oxime was prepared according to the directions given by Windaus, and was obtained from ethyl acetate in needles which melted and decomposed at 191° :

0.1794 gave 0.4928 CO_2 and 0.1802 H_2O . $C = 74.86$; $H = 11.16$.
 $C_{26}H_{43}O_3N$ requires $C = 74.75$; $H = 10.38$ per cent.

This acid formed a beautifully crystalline *potassium* salt.

On oxidising the keto-acid with potassium hypobromite, an acid was obtained which after crystallisation from benzene sintered at 127° and melted at 130° with gas evolution. It was deliquescent. On titration:

0.2240 required 14.0 c.c. $N/10$ sodium hydroxide. Equivalent = 160.
 $C_{26}H_{42}O_6$, tribasic, requires 150.

The keto-acid therefore on further oxidation gives the tricarboxylic acid $C_{26}H_{41}O_6$.

In all these particulars our acid corresponded with the ketomono-carboxylic acid described by Windaus.

Action of Ozone on Cholesterol.—Ten grams of anhydrous cholesterol were ozonised in chloroform solution as described above. The product was purified by solution in ethyl acetate and precipitation with light petroleum. It dried in a vacuum to a perfectly transparent glass which readily powdered. It had all the properties of an ozonide. When heated on platinum it enflamed, and it liberated iodine from potassium iodide solution:

0.1796 gave 0.4896 CO_2 and 0.1697 H_2O . $\text{C} = 74.35$; $\text{H} = 10.44$.

$\text{C}_{27}\text{H}_{46}\text{O}_2$ requires $\text{C} = 74.66$; $\text{H} = 10.55$.

It thus appears that the ketone is monovalent, and contains three atoms of oxygen at the ethylene linkage of the alcohol in a normal manner.

Rotation.—0.9647 gram made up to 25 c.c. with chloroform gave a $+1.12^\circ$ in a 2-dcm. tube; hence $[\alpha]_D^{25} + 14.51^\circ$. The rotation of cholesterol is $[\alpha]_D^{25} - 36^\circ$.

On treatment with water in a manner similar to that described under cholestenone, the aqueous distillate had an odour of orange oil, was acid, and after neutralisation and evaporation gave a little solid matter which strongly reduced ammoniacal silver solution and probably consisted of barium formate. In the absorption vessels containing the baryta a copious precipitate of barium carbonate was formed, which was collected and identified in the usual way. The water remaining in the flask was milky. It was acid, and gave the magenta test for aldehydes. The solid left was a brown resin, which dissolved in alkalis and gave precipitates with salts of the heavy metals. We have, however, not as yet been able to separate any of the constituents in a state of purity, but we are carrying out other experiments on derivatives of cholesterol which we hope will throw some light on these compounds.

Conclusions.

These experiments on cholestenone fully confirm the hypothesis of Windaus that this ketone contains an unsaturated side-chain with the double link in a vinyl group. If the relationship of cholestenone to cholesterol is that of a simple ketone to its secondary alcohol; then the latter substance must contain a similar unsaturated side-chain. This is confirmed by our observation that cholesterol forms an ozonide, which on decomposition with water yields carbon dioxide. Direct experimental proof of this point has hitherto been lacking if we except the somewhat complex reduction of cholestenone to cholesterol through an isomeric β -cholesterol, recently carried out by Diels and Linn (*Ber.*, 1908, 41, 260).

The expenses of this work have been defrayed by a grant from the Royal Society, for which we take this opportunity of expressing our thanks.

PHYSIOLOGICAL LABORATORY,
UNIVERSITY OF LONDON.

CXXVIII.—*Apparatus for Experiments at High Temperatures and Pressures, and its Application to the Study of Carbon.*

BY RICHARD THRELFALL, F.R.S.

EXPERIMENTS at high pressures have generally been made by employing a gas or liquid to communicate pressure to the substance under examination. If the latter has to be heated, compressed gases have usually been preferred, although Parsons (*Phil. Mag.*, 1893, [v], 36, 304) describes some experiments in which carbon rods were heated under a pressure of from 5 to 15 tons per sq. in. in various liquids. The possibility of using substances which are considered as solids at atmospheric pressures is suggested by Spring's researches, but that a sufficient degree of fluidity might be expected for the accurate inference of a definite hydrostatic pressure was not superficially obvious. Spring mentions that crystalline graphite flows very easily under high-pressure differences, and, indeed, its properties are such as to raise an expectation that if any solid could be used as a means of bringing hydrostatic pressure to bear measurably during an experiment, that solid would be graphite.

I was anxious to test the matter, and arranged the following experiment, employing some apparatus that happened to be at hand.

A steel rod was bored for some distance to a diameter of half an inch (12.7 mm.), and this hole was continued by one of 3 mm. diameter and 15 mm. long. The wider tube was then filled with Ceylon graphite in its natural state, and, a ram having been fitted, the apparatus was placed in a simple hydraulic press provided with a pressure gauge, and an attempt made to ascertain the pressure necessary to force the graphite through the 3 mm. tube. The pressure gauge had a dial six and a half inches in diameter, and was graduated up to eight tons pressure per sq. in. From the relative dimensions of the press and experimental rams, it was calculated that a reading of one ton per sq. in. of the gauge corresponded with a pressure of 62 tons per sq. in. on the graphite. From the experiments of A. Martens (*Zeitsch. Verein. Deut. Ing.*, 1907, 51, 1184; *Science Abstracts*, 1907, 10, 522), it appears that the cup leather friction of a press introduces errors in the load estimated from the gauge pressure to an extent of less than 2.5 per cent. On applying pressure, the graphite streamed through the round tube as a solid

wire before any indication of pressure was given by the gauge, not the slightest tremor being perceptible. The pressure was of one-fiftieth of a ton per sq. in. and the flow was not perceptible. In the application of the force of graphite, it is probable that not one-hundredth part of the resistance to flow offered by the 3 mm. tube would be presented, and it is therefore accepted that for the apparatus in question solid graphite might be regarded as a frictionless fluid.

On repeating the experiment with a plug of amorphous graphite prepared by the Acheson process, it was found that the pressure as indicated by the gauge rose to one ton per sq. in. before flow took place, that is, that about 60 tons per sq. in. were needed to make the graphite flow through the tube. The fluidity of crystalline graphite, therefore, enables experiments at high pressures and temperatures to be carried out easily by simple laboratory appliances, and renders it unnecessary to use compressed gases, whereby an enormous saving in cost of apparatus is obtained, and much greater freedom from danger is secured.

It was an interesting question whether graphite, which has been made to intumesce by treatment with nitric acid and potassium chlorate, and subsequent heating, would flow as easily as unheated crystals. So far as the apparatus described can show, there is no difference between ordinary and intumesced graphite. The intumescence of graphite is generally explained on the basis of there being an assumed oxidisable material distributed between the flakes of the crystals; if this be true, the subdivision must be very minute, for some graphites can be intumesced into a very finely-divided state. This property renders it very favourable for purification by fusion with alkalis, and treatment with hydrofluoric and other mineral acids. Moissan, in his exhaustive article on graphite (*Traité de Chimie Minérale*) does not mention the advantage of intumescent graphite before treating it with alkalis and acids for purposes of purification.

Spring notes that powdered substances differ very much in their power of flowing under high pressure, a fact which I have often confirmed. Silica, even in the finest state of division, practically does not flow at all; and the same property characterises magnesia, which, after purification and fusion by electrical means, followed by fine grinding and sifting (240 threads to the inch run), will support a pressure of over 50 tons per sq. in. without being consolidated for more than a few mm. below the ram. The case of alumina is interesting. Aluminium hydroxide, as it occurs in commerce, is a fine granular powder, each granule, under the microscope, being seen to consist of a number of small crystals. Alumina is, of

course, the result of calcination, but the alumina produced from the granular hydrate is a granular mass, each grain being made up of the pseudomorphs of the hydrate. When alumina in this form is pressed, the grains will not flow, but will form a fairly coherent mass, and it is easy to make small objects by compressing the alumina in suitable moulds, no binding material being necessary.

Therefore, on the one hand, we have in graphite a conducting fluid under high pressures, boiling only at a very high temperature, and, on the other, non-conducting, rather infusible substances which can be consolidated by pressure, in which state they are practically incapable of flowing. The construction of apparatus in which these two sets of properties can be utilized is, of course, obvious.

Nevertheless, several forms of such apparatus which have been experimented with were found to be faulty in some particular or other, and the apparatus, as figured, although it may appear to be the simplest possible, was only arrived at after some failures.

The apparatus consists of three parts:

1. Appliances for producing pressure.
2. A vessel capable of withstanding the pressure.
3. Apparatus for electric heating.

The most convenient way of producing pressure in the laboratory is by means of a hydraulic lifting jack. It is necessary to provide an iron frame against which the jack can work. A jack to lift 50 tons is usually quite large enough (see Fig. 3).

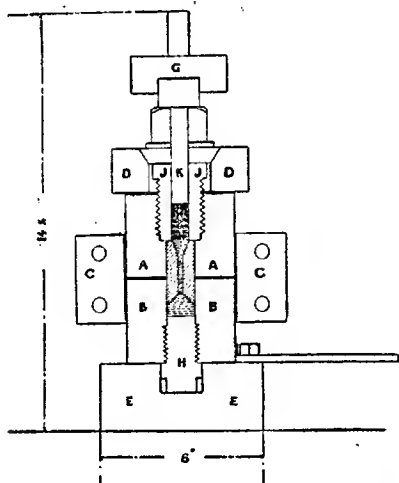
The electric heating is most conveniently provided for by a 10 or 20 kilowatt transformer, wound on both sides with several separate windings, which can be connected up so as to suit the requirements of different experiments.

The pressure vessel is illustrated as applied to the heating of a carbon rod. It consists of two cylinders of high-grade steel, A, A, B, B (Figs. 1 and 2). In the actual case, these cylinders were made of Vickers' "C. 10" special tool steel, used in the fairly soft condition in which it was supplied; gun steel might be better. Each cylinder is turned and ground to exactly the same external diameter, and the faces which are intended to be in contact are finished by grinding, so that they fit with almost optical precision. This is essential to success. Each cylinder is bored as shown; and, after the cylinders are clamped together by the carefully turned clamps, C, C, the hole is ground out to a truly cylindrical form. The clamp is separated from the metal cylinders by a thin sheet of presspahn of uniform thickness, and in boring the clamp allowance is made for this. The two metal cylinders are separated by a sheet of mica

about $\frac{1}{2}$ mm. thick, and the sharp edges of the hole are chamfered off to the extent of about 0.5 mm. at each side of the mica sheet. The cylinders are held together from end to end by means of the cross-pieces, *D,D*, *E,E*, and the bolts, *F,F* of mild steel. The reason for making the pressure vessel in two insulated parts is that the walls of the vessel may be at nearly the same potential as the heater where it is nearest to them; also it is a great convenience at the termination of an experiment to be able to break into the vessel at the point where the reaction to be investigated has taken place, for then the result can be seen *in situ*.

The bottom cylinder is provided with a screw plug, *H*, the head

FIG. 1.

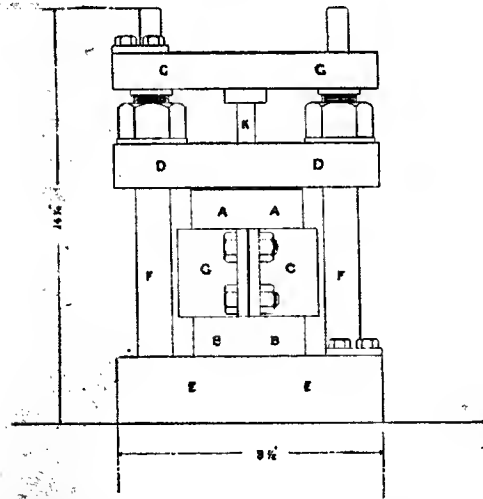


of which is let into a recess in the bottom plate, and it is so arranged that the head of the plug comes into contact with the bottom plate, the lower cylinder being just clear before pressure is applied; in this way the pressure comes directly on the plug, and the screw threads are not strained by the pressure, so that the plug screws out easily at the end of an experiment. The plug is of hardened tool steel; anything else will "set up" in the threads, and then the plug cannot be withdrawn.

The upper cylinder is also provided with a plug of hardened tool steel, *J*, with the end accurately ground so as to fit the bottom of the recess. If this precaution be omitted, graphite is forced up from under the plug and causes it to jam. Several plugs may be

provided, bored for rams of different diameters, so that different pressure intensities may be transmitted. The ram *K* is made of the highest quality hardened tool steel, and fits at the top against a piece of hardened steel let into the insulated bar *G*. The tops of the holding-down bolts, *F, F*, are turned to fit two holes bushed with fibre in the bar *G*. This ensures the application of the pressure to the ram exactly in the direction of its length, a most necessary precaution, even when the ram is well guided by the sides of the hole in the plug *J*, which, of course, is a close fit. The slightest indirectness in the application of the force to the ram causes the sharp edges of the lower end to dig into the steel plug. It is

FIG. 2.



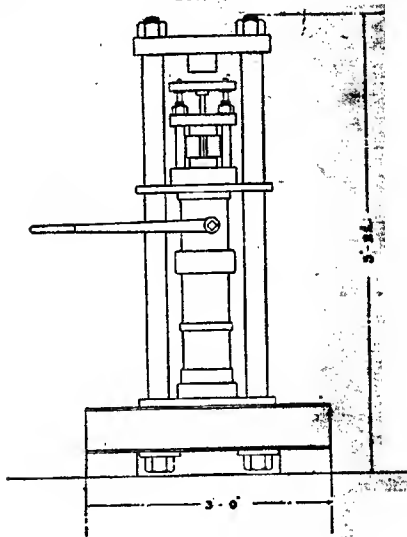
obvious that the ram must be ground to fit the bore of the plug exactly, otherwise graphite escapes at the sides, and tends to jam the ram, so that the internal pressure becomes uncertain.

The electrical connexions are made as follows:

It has been mentioned that the two halves of the pressure vessel are insulated from each other by a sheet of mica. The pressure vessel is also insulated from the upper clamping bar by a disk of mica placed between the upper half *A* and the clamp *D*. The current enters the apparatus through the bar transmitting pressure to the ram, and thus the bar, ram and upper cylinder *A* are all at practically the same potential. The current leaves by a connexion to the plate *E*, whereby the lower cylinder is brought to the poten-

tial of the point at which the current leaves the ram. The full potential difference is applied between the cylinders 4 and 5. If the cylinders are left sharp it is found that an arc tends to form between them for this reason they are chamfered off, as stated. The apparatus is mounted in a rectangular frame as shown, the apparatus lifting jack being placed below the pressure vessel. The top of the jack is guided by a plate provided with two holes, through which the main bolts pass. In order to save the trouble of tooling these

FIG. 8.



bolts, it is convenient to pass them through sleeves of drawn brass tubing.

In the arrangement shown, the pressure vessel is lifted against the ram as the pressure comes on, and some flexibility is therefore required in electric or water connexions.

Preparation of Pressure Vessel for an Experiment.

It has been stated above that silica, magnesite, and alumina in fine powder can be consolidated under heat and pressure, provided that not more than about 3 mm. thickness of material is consolidated at one time. If it is intended to make use of carbon as

a resistor, magnesia is to be preferred for obvious reasons, although possibly porous graphite would do as well or better (Heraeus, D.R.-P. 187,000).

There are several ways of obtaining pure magnesia free from impurities, but at all events, in any of several samples which were examined, lime was found. The most effective method of separation of lime from magnesia appears to be that indicated by Sonstadt (Crookes, *Select Methods*, 1871, p. 39), in which the lime is precipitated by sodium tungstate from a slightly ammoniacal solution. When really pure magnesia is required, it has been found economical to start from magnesite and commercial hydrochloric acid, but the obvious details do not require further reference; it is, of course, necessary to guard against the presence of silica. For many purposes, where a trace of calcium or silicon carbide does no harm, the "pure magnesia" of commerce can be obtained of sufficient purity. However the magnesia may be obtained, it must be calcined before electric melting, otherwise so much water vapour is given off that a considerable quantity of the fine powder is blown away. The magnesia may be fused either by a smothered arc between carefully-purified graphite electrodes, or, with less chance of contamination, by means of a graphite rod with water-cooled connexions, as in the well-known process of preparing fritted sand-tubes.* The dense, fused product, which should be perfectly white, is ground in a hard steel mortar and sifted through the finest silk or wire sieve, say, 170 to 200 threads to the inch. The particles of steel from the mortar are collected by a pointed electro-magnet, with which the powder is stirred until nothing more is extracted. A considerable amount of stirring is necessary. A good deal of time may be saved by preparing enough magnesia for several experiments at one operation.

The pressure vessel is lined with magnesia in the following manner. The ram and upper plug of the apparatus are removed, and a temporary plug bored to the internal diameter of the pressure vessel is screwed in its place. A hard steel ram is provided to fit this plug exactly, and long enough to pass to the bottom of the pressure vessel. Unless the steel is of good quality, and very hard, it will "set up" under pressure, and become so tightly wedged in the apparatus that it cannot be withdrawn. Vickers' "C. 10" steel has given good results in this and similar cases, the ram, of course, being ground after hardening.

A plug of Achard's ordinary graphite is turned to fit the bore of the pressure vessel, and provided with a conical end. This plug may be boiled out with hydrochloric acid if the presence of a little oxide of iron is an objection, but the process is a long one. In

any case the plug must be heated to redness shortly before being placed in the vessel, where it forms the bottom of the reaction.

The magnesia powder is added in small quantities at a time, and consolidated under a pressure of about 400 lb. per sq. in. (approx.), only enough magnesia being added on each occasion to correspond to a cake of about 3 mm. thick; after each pressing, the surface of the magnesia is scored by a hard steel point, and the pressing continued until the vessel is full to a little above the bottom of the upper plug. This plug is then unscrewed, and the whole apparatus removed to a lathe, where it is mounted so as to rotate about the axis of the cylindrical plug of magnesia. The magnesia is then drilled by a hard steel twist drill 3 or 4 mm. in diameter, the upper end being opened out to a conical mouth. The top of the magnesia tube is carefully levelled to the level of the bottom of the proper plug, which is then placed in position and screwed home by a special key. Graphite, purified in accordance with the end in view, is then introduced, and rammed by hand into the magnesia tube, and, finally, the graphite filling is continued about half-way up the plug, so that a reservoir of graphite may be present to be drawn upon as required.

Finally, the ram is inserted, and the graphite pressed up with more than the full pressure it is intended to use. A heavy current (five or six hundred amperes for a 3 or 4 mm. hole) is then passed through the graphite, and in a few seconds the pressure gauge shows that the pressure is beginning to fall, owing to the melting of the magnesia, for however tightly the powder be packed, it will be found to make more room for the graphite when it melts. The current is kept up for five or six seconds (details of a particular trial will be given later), and the pump is worked vigorously to keep up the pressure, which continues to fall after the current is turned off. If the operation is done with the judgment which a little experience easily gives, the magnesia lining is converted into a tube of fused magnesia extending to within 2 or 3 mm. of the steel walls. Unfortunately, it seldom or never happens that the bore remains uniform in diameter, but this does not greatly matter. The apparatus is allowed to cool *in situ*, and then the ram is pulled out; two facets ground on the upper part of the ram are convenient for allowing a key to be used to twist the ram to loosen it. The graphite, unaltered except that it is now softer and more crystalline, as described by Parsons (*Proc. Roy. Soc.*, 1907, 79, A, 532), is scraped out, and the mixture on which it is desired to experiment introduced, the conical opening of the magnesian tube being then packed with graphite as before. If the mixture is a non-conductor, a conducting rod or wire of suitable material is introduced as a

heater with the charge. The desired experiment can then be made, and it is found that the rammer tube has no longer any considerable tendency to expand in diameter.

The advantage of the particular construction described, in which the pressure vessel consists of two insulated parts, lies in its freedom from accidents due to the penetration of filaments of graphite through the walls, causing short circuits when they strike the sides of the vessel. These filaments may be produced as described by Watts (*Trans. Amer. Electrochem. Soc.*, 1907, 11, 9279).

Before the construction described was arrived at, quite sharp explosions of iron vapour from the vessel were of frequent occurrence owing to this cause. It will be sufficiently obvious that the whole of the design depends on the use of a considerable quantity of graphite as a means of transmitting pressure from a comparatively cool region, where the cross-section of the graphite is large, to a hot one, where the cross-section is small. Before this device was hit upon, a great many experiments were made in an apparatus similar to the one described, but in which the pressure vessel consisted of a single piece of metal. In this construction, graphite and copper wads were used to conduct the current from the bottom of the ram to the heater of much smaller cross-section. Various ways of forming the insulating lining of the tube were tried. One of the earliest was to build up a tube by sheets of clear mica wrapped round a mandrel of rather less diameter than the ram. The tube and mandrel were then pushed into the cylinder, and the mandrel slightly untwisted, when it could be withdrawn. For temperatures up to a red-heat this gives a satisfactory lining, but if copper washers are used to protect the end of the ram from contact heating, it is found that the copper almost invariably cuts through the mica by lateral expansion when the pressure is put on.

In all constructions of apparatus, or arrangement of experiment in which a considerable rise of temperature is to be expected at the screwed plugs, these must be made of high-speed steel, and water-cooled. The same precaution has to be taken with the ram. In both cases care must be taken that the bottoms of whatever holes are drilled in the steel for water-cooling are nicely rounded, and not left conical from the drill, as the risk of cracking during hardening is thereby diminished.

There is no difficulty whatever in carrying out a system of water-cooling, and "high-speed" steel was a great improvement on ordinary tool steel in regard to freedom from expanding laterally under heat and pressure. The question as to the behaviour of carbon was really settled in such an apparatus before the improved form was arrived at; the advantage of the latter lies in its sim-

plicity and in the ease with which massive experiments can be carried out in it.

In researches in which the pressure (see above) has to be maintained for more than a few minutes it still be found convenient to make both the ram and the pressure steel, and to make use of water-cooling. A ram of tool steel, 13 mm. in diameter, was bored to a diameter of 10 mm., the depth from the hemispherical crown of the bore to the top of the ram being 3.5 mm. This ram carried a pressure intensity of 109 tons per sq. in. without yielding or breaking, and was used in a successful experiment. It is perhaps as well to add that the instructions issued by the steel-makers in regard to hardening and tempering the steel were rigorously followed.

The main difficulty encountered throughout was in regard to the porosity of the lining of the pressure vessel. It was found to be very difficult to fill the bore with magnesite in such a way that soft spots did not occur here and there, through which hot graphite was forced by the pressure. Many attempts were therefore made to arrive at a more solid form of lining, with the following results. A tube of alumina from calcined hydroxide was more solid than the magnesia tube, but was so hard that it could only be drilled (by steel) with the greatest difficulty. The carbon rod used as a heater was separated from the alumina by a layer of magnesia rammed round the rod by a tube-shaped ram. The result was fairly satisfactory. Attempts were also made to make tubes in other moulds, cut them out round the outer circumference, and grind them until they fitted the pressure vessel. The trouble involved was very great, and no real improvement resulted. It was found impossible to avoid the boring out by using a tube-shaped ram to compress the material round a taper mandrel, because the mandrel, although of the hardest steel, and accurately ground and polished, could not be forced out.

The consolidating power of magnesia is improved by mixing a little fine graphite with it and sifting the mixture to great uniformity of composition. To attain this, the graphite has to be present in sufficient quantity to make the resulting tube appreciably electrically conducting. Addition of oil did not cause the magnesia to make the tube more free from soft places, but it made the work of compressing the magnesia in the vessel, removing the temporary ram, &c., more easy.

China clay did not make a better tube than magnesia. It was noticed incidentally that a mixture of dry china clay and paraffin oil has not the plastic properties of a mixture of china clay and water. This is of interest for the theory of plasticity, but it is

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difficult to believe it is not generally known, although it was new to me.

Most of the tubes made from compressed amorphous silica of about 1000 psi. One was broken with a mandrel having a lining made of ground metal sand. Although the tube was ground to be a close fit, it broke directly the pressure was on.

Tubes made from compressed amorphous silica, alone or mixed with ground felspar, were unsuccessful and difficult to bore.

Experimental.

It may be stated at once that the results obtained with carbon differ in no respect from those already published by Parsons (*Proc. Roy. Soc., loc. cit.*) in so far as they cover the same ground, but as Parsons has not published any details of his experiments, I think it desirable to place my data on record, for which it will suffice to select some typical trials.

Experiment 7, September 13, 1906.—Apparatus: Pressure vessel made in one piece, with water-cooled rams and plug.

Graphite washers (Acheson's), 7 mm. thick, were placed between the ram and the heater.

Area of ram of hydraulic press, 9.62 sq. in. = 62.05 sq. cm.

Diameter of ram of pressure vessel, 1.3 cm.

Area of ram of pressure vessel, 1.33 sq. cm.

Pressure produced in vessel per ton per sq. in., as shown by Bourdon gauge, $62.05/1.33 = 46.65$ tons/sq. in.

Actual pressure probably 2 per cent. less, say 45 tons per sq. in. per ton shown on gauge.

Lining of pressure vessel, magnesia purified from lime by sodium tungstate, and ignited in injector furnace at a temperature at which the fireclay crucible softened and settled.

Thickness of walls of compressed magnesia round ram, 3 mm.

Thickness of walls of compressed magnesia round carbon heater, 7.5 mm.

Carbon heater 33 mm. long, 4 mm. diameter.

The heater was turned down from a small rod of electric light carbon, which had been treated with boiling hydrochloric and hydrofluoric acids, and ignited. The calculated electric resistance of the rod is 0.13 ohm cold.

The current employed for this experiment was low periodicity alternating current at about 100 volts. The alternator circuit included an electrolytic resistance of a solution of sulphuric acid between lead plates hanging in a tub. The pressure vessel terminals were short-circuited by a large switch, which could be opened when it was desired to start the current, and the resistance

of the electrolytic regulator was so large compared with that of the pressure vessel that the current was only slightly increased by opening the switch. This enabled the pressure to be raised quickly.

The press was pumped to a gauge pressure of 20 tons per sq. in., which is equivalent to a maximum pressure of 11.7 tons per sq. in. in the pressure vessel, neglecting friction losses. The pressure gauge employed was a new one, passed as accurate by the makers, but not tested by me for want of suitable appliances, although I have no reason to suspect there was any appreciable error in its indications. The pressure was transmitted by graphite from the 13 mm. ram to the carbon heater.

The current was turned on for five seconds at a mean value of 300 amperes. The voltage was not obtained, the voltmeter being unsuitable for rapid reading. If the resistance is taken at 0.15 ohm at first, and the inductance is negligible, the voltage would be 45 volts, and the power 13.5 kw.

During the five seconds, the pressure as shown by the gauge did not give way at all, although the current density was about 24 amperes per sq. mm. of carbon section. The apparatus was then allowed to cool down for four minutes, the ram and plug being cooled by the circulation of a vigorous stream of water.

The switch was again opened, and 400 amperes passed for four seconds, when an explosion occurred, and the current was stopped; the pressure fell off, and may be regarded as of the order of a few tons per sq. in. during the cooling. The contents of the pressure vessel were removed by cutting away the magnesia round the rams (which in this trial entered from both ends) and then pushing out the central part, including the carbon rod, by means of a larger ram and the hydraulic press. The explosion was found to have been due to a short circuit between the upper ram and the side of the pressure vessel through a presumably soft spot in the lining. A piece of the core, weighing 0.0774 gram, had not been affected by the explosion, and was examined. It was found to be a fine-grained graphite. The porosity was tested by saturating it with water by long boiling and exhaustion in a vacuum under water, and it was found that the weight had increased to 0.0782 gram; on drying and heating to a red-heat a weight of 0.0773 gram was recovered. The gain in weight due to absorption of water was therefore only 1.164 per cent. of the weight of the dry graphite. A similar experiment, carried out on a small piece of artificial (Acheson's) graphite, showed a gain in weight of 8.08 per cent. Some intumescent graphite was compressed with a load of 25 tons per sq. in. without heating, and in this case water was absorbed to the extent of 5.9 per cent. of the weight of the original graphite.

The slight porosity was quite in keeping with the observed hard-

ness and fineness of grain of the graphite. The microscope showed that the graphite consisted of masses of minute felted crystals, the granular appearance of the original carbon being quite lost. The magnesia surrounding the carbon had the appearance of having been melted; it was black, and, under the microscope, was seen to consist of a mass of fused or partially fused material thoroughly injected with filaments of graphite. On boiling the magnesia with water, no odour of acetylene could be detected, but on heating with sulphuric or hydrochloric acid, a decided odour of acetylene was noticeable; the action even of boiling sulphuric acid (say 50 per cent.) is slight. The odour perceived was slight, and was attributed to traces of the carbides of calcium and iron, the latter being present in measurable quantity, and it was most likely introduced by the ramming and drilling-out process which the magnesia had undergone. Prolonged action of hot concentrated hydrochloric acid left a mass of graphite crystals, but it was not absolutely proved that these came from the heater and not from the graphite used as a pressure transmitter; but from the close contact between the heater and the magnesia rammed round it, it is highly probable that these crystals come from the heater. It is interesting to note that even at this temperature and pressure no magnesium carbide appears to be formed, or at least to persist. The above observations on the state of the magnesia apply essentially to all the trials made.

Experiment 8, September 20, 1906.—The conditions of experiment 7 were exactly reproduced, except that the current of 580 amperes was kept on for two and a half to three seconds only. The voltage at the end was a good deal above 6 volts, but less than 20 volts, probably about 12 volts.

The pressure did not yield at all during the trial, and was kept at 117 tons per sq. in., less, say, $2\frac{1}{2}$ per cent., due to cup leather friction, throughout the cooling.

Assuming that the voltage and current are coincident in phase, which must have been almost exactly the case owing to the low period, and large resistance in circuit, we can form an idea of the energy supplied. Taking 10 volts, 2.5 seconds, 580 amperes, we have 5.8 kw. for $2.5 \times 14,500$ watt seconds = 3,450 calories. The carbon weighed about 0.75 gram.

Vielle (Landolt and Börnstein, *Tabellen*) gives the specific heat of graphite between 0° and 2000° as 0.475, and from 0° to 3000° as 0.535. Dewar gives 0.314 for gas coke from 0° to 1040° . If we take the largest of these values, and assume that the heat put in an apparatus during the two and a half seconds in which the temperature through which the carbon is raised is $175 \times 0.535 = 8600^\circ$.

No doubt a great deal of heat is lost to the magnesia, but on the

other hand we have taken what is probably a minimum value for the energy supplied, so that there is no doubt that a very high temperature was attained. The pump takes, say, 400 watts in the air, so that the energy supply is sufficient to keep eight lamps going for more than 0.5 c.c. of carbon for a period of two and a half hours at least. Also, there is no doubt as to the pressure having been kept on the rams, as the gauge did not move, and an assistant was exerting his whole force on the pump lever all the time. There is, however, a possibility that some of this pressure might have been taken up by the edge of the magnesia packing surrounding the carbon rod, and by the graphite forced between the ram and the magnesia tube. It is improbable, however, that more than a small percentage of the pressure intensity was taken up in either of these ways.

At the end of the experiment the rams were removed by cutting out the magnesia, and the central part was pushed out in the press. The carbon was converted wholly into a hard, dense graphite, as in experiment 7. The magnesia tube had the same appearance, and was in every way similar to the tube described in connexion with that trial.

Experiment 9.—Apparatus as in experiments 7 and 8. Current, 550 amperes, between 15 and 20 volts, for four seconds. The pressure gauge at the beginning of the heating showed a pressure of 2 tons per sq. in., giving 93.3 tons per sq. in. in the pressure vessel, if no allowance is made for friction. On starting the current the pressure dropped to $1\frac{1}{2}$ tons per sq. in., but pumping brought the reading back to its initial value before the current was stopped, and this pressure was maintained for ten minutes afterwards, so that there could be no question as to the pressure under which the carbon cooled. Taking the lowest possible value for the voltage, namely, 15 volts, we have an energy supply of 8.25 kilowatts = 1.95 kilogram-calories per second, or 7.8 kilogram-calories in the four seconds. At the close of the experiment the magnesia was cut away and the core pushed out. It was found that the magnesia had been fused for about 1.5 mm. round the carbon, and sintered for 1.5 mm. more, but beyond this point it was unaltered. The sintered magnesia was removed by grinding, as was the fused magnesia on one side of the core. The fused magnesia then broke longitudinally, and there was extracted a conical shaped fragment, 10 mm. long, and 7 and 3 mm. diameter at the two graphite ends respectively. The sides of the graphite block showed graphite having moved relatively to the magnesia envelope; the surface was, in fact, the "skinside." There were

some nodules of harder graphite projecting into the magnesia. In this experiment, as in many others, it was noticed that where the carbon residue was most abundant, the graphite it had been derived from was harder than elsewhere, and the graphite fragments that had been separated were much harder at the ends than elsewhere. The hardness was such that a file only just scratched it, and it did not appear to be carbide, as water had no action on it. Owing to the presence of impurities in the Acheson graphite, and, consequently, want of certainty as to what might have taken part in the reaction, this hard part was not further examined. The main fragment was very soft graphite, marking paper more softly than the softest drawing pencil. The porosity was determined by exhausting under boiling water as described in connexion with experiment 7, and it was found that water was absorbed to the extent of 0.069 gram by a piece weighing when dry 0.546 gram, that is, a gain in weight of 12.64 per cent. of the dry weight. The density of the graphite was determined by testing pieces of one to two cubic millimetres volume in potassium and mercury iodide solution, the density of the liquid being afterwards measured in a Sprengel tube. The liquor and pieces of graphite were exhausted and heated together until constant readings were obtained.

The result was that at 15° the density was 2.240. The hard part had a density of 2.12, and the unaltered Acheson graphite 1.95. The possession of porosity is, I think, remarkable, having in view the heavy pressure under which the graphite was crystallised. 2.24 is about the figure recently given by Le Chatelier for all graphites when properly exhausted. Using this value it is seen that a piece of graphite weighing 0.546 gram was able to absorb 0.069 c.c. of water. If graphite had filled this space it would have weighed 0.155 gram, or the ratio of the volume of graphite crystals to pores is in the proportion of 100 to 28.3. In view of the easy fluidity of graphite under high pressure, it was difficult to believe that the pressure was really being transmitted properly to the graphite, which was crystallising, and it seemed possible that the ram was being supported partly either by the edge of the magnesia when this solidified, or by graphite wedged in between the ram and the magnesia tube, although it is certain that the pressure was very high. To meet this difficulty the design of the apparatus was altered, and the apparatus as illustrated was the outcome of this modification. While the new apparatus was being prepared, some further trials, similar to those described, were carried out in an apparatus in which the outer lining was ignited compressed alumina. This made a harder tube, but one not really so sound as the magnesia, and

several explosions occurred, breaking the rams. It was also more difficult to keep up the pressure. However, the results obtained, so far as they went, were identical with those already described, and the same remark applies to some trials in which unpurified natural graphite was employed. Except that the graphite crystal formed from the natural graphite were, if anything, rather larger than those coming from the amorphous carbon, and that the heating could be more prolonged at constant current, owing to the lower resistance of the core, no difference in the result could be detected. In one case a supply of 60 kilogram-calories was accomplished in 10 seconds, but the pressure could not be maintained owing to the flow of molten magnesia. The product in this case was brilliantly crystallised graphite. The graphite was destroyed by Brodie's nitric acid and potassium chlorate mixture, as described by Moissan, a separation of the residue by a heavy liquid was carried out, and a search for diamonds, made by the microscope, but none were found. On fusion with potash in a silver spoon, the residue entirely disappeared.

Experiment 14.—Apparatus, as figured, with one ram, water-cooled. Material, unpurified natural graphite. The tube was pure fused and ground magnesia, from which the iron had been extracted by a magnet.

Dimensions of narrow part of heater: Length, 57 mm.; diameter, 4 mm.

Current, 500 amperes, 65 volts, for six seconds.

Calculated pressure in vessel, 48.5 tons per sq. in. per "ton per sq. in." shown by gauge, uncorrected for cup leather friction.

Initial pressure, 48 tons/sq. in.; at the end of six seconds the pressure fell to half this amount, and did not return to its initial value until five seconds later; during this time the average pressure was about 36 tons/sq. in.

Energy supply (volt-amperes), 46.8 kilogram-calories.

Taking the density of the graphite at 2.2, the weight of graphite in the narrow neck was 1.58 grams.

After cooling, the pressure vessel was taken apart, showing a section of the graphite *in situ*. The diameter of the graphite core was now 8 mm., and the magnesia had melted round it to a diameter of 11 mm. It was fused to a diameter of 15.5 mm., leaving the remainder unaltered; the diameter of the bore was 25.5 mm. The magnesia tube was pushed out of the vessel, and it was seen that the graphite was no longer in the form of a cylindrical rod, but was of much greater diameter in the centre (where the temperature had been highest). As before, the part in contact with the Acheson graphite plug was found to have penetrated the latter

to a depth of several mms., and this part was extremely hard. The hard part was prepared for diamond in the usual way, but not the slightest diamond could be found. The main body of graphite was reduced to small, irregular and brilliant crystals.

Experiment 15.—Essentially a repetition of the last experiment, but purified graphite was used. This was made by heating a quantity of Ceylon graphite to intumesce, covering the intumesced product with a concentrated solution of potassium hydroxide, and evaporating the mixture down to a fusion at a red heat for about two hours. The potash was then dissolved out, and the residue treated several times in succession for some hours at a time with hydrofluoric and hydrochloric acids, and, finally, with hydrofluoric and sulphuric acids.

The graphite was washed free from acid, dried, and ignited in a crucible. During the fusion with potash a slight further intumescence was noticed.

The energy supply was 450 amperes, at 55 volts, for 4.5 to 5.0 seconds. The pressure did not fall at any time below 36 tons per sq. in., and was, on the average, about 50 tons/sq. in (uncorrected). The magnesia was fused for a distance of 3 mm. from the core, at the centre of its length. The core was practically all oxidised by Brodie's reaction, and, so far from there being any diamond, nothing could be collected for separation by the dense liquid. The part of the core which penetrated the artificial graphite was again seen to be very hard.

An experiment was made to test whether the graphite could jam the ram, but it was found that when the graphite was allowed to escape by having the two halves of the pressure vessel insufficiently pressed together, the graphite was forced out without the gauge showing any indication of pressure.

Experiment 16.—The reaction (Tone. Am. Patent, 833427) $\text{Fe} + \text{SiC} = \text{FeSi} + \text{C}$ was verified to some extent in an ordinary smothered arc furnace, although the yield of silicide was small.

The product was not analysed, but was recognised as having the composition FeSi_2 , not FeSi , by its resistance to 25 per cent. nitric acid, and reacting violently with hydrofluoric acid (Moissan, *Four. Elect.*, 347).

On carrying out the reaction under pressure, only graphite was found, but the iron was distributed in such a way as to suggest that it had been melted and forced into the magnesia tube before the temperature of reaction was reached.

The apparatus as described was entirely constructed by my assistant, Mr. C. H. Beasley, and the experiments were also prepared by

him. Assistance in purifying materials and examining products was afforded by Mr. T. H. Waller. I desire to acknowledge my indebtedness to these gentlemen. The experiments were in all cases conducted by myself.

Note on the Examination of the Products of Reaction.

The method of Prod'homme with Moissan's slight modification [*Electric Furnace* (*Proc. of the Royal Soc. Trans.*), p. 49] was used throughout, although Staudenmaier's method (*Ber.*, 1898, 31, 1485) is more convenient for the preparation of considerable quantities of graphitic acid. It was not expected that small crystals of diamond would be formed, as the conditions of experiment were at all events intended to be adjusted so as to give a complete transformation to the greater part of the graphite treated, had it so happened that this was possible. Nevertheless, for the sake of completeness, the treated graphite was regularly searched for minute diamonds. Of course nothing can be done until the graphite is destroyed, and as this is the most lengthy part of the process it is important to be able to see when the transformation to graphitic acid is complete. After the first attack by nitric acid and potassium chlorate, the colour of the graphitic acid is so deeply green that it is not easy to see whether particles of untransformed graphite are left or not. A difficulty in regard to washing the graphitic acid is mentioned by Staudenmaier and has been confirmed, namely, that much washing tends to make the graphitic acid slimy and difficult to handle.

Staudenmaier's treatment by potassium permanganate and subsequently by hydrogen peroxide was found of service in removing the green colour. Deflagration of the washed and dried graphitic acid must be done very carefully in a deep beaker and little by little, as the deflagration is quite sudden enough to cause risk of the ejection of fine particles. After the deflagration is complete, it is best to wet the residue thoroughly with nitric acid (acid of sp. gr. 1.4 may be used), then add a mixture of one volume of nitric acid to two volumes of strong sulphuric acid, cool, and cautiously throw in crystals of potassium chlorate to the extent of twenty times the weight of the graphite originally taken. It is obviously necessary to keep the liquid cool by adding the chlorate gradually, the beaker standing in water meanwhile. In about two hours the pyrographitic acid is dissolved, and any traces of graphite that have been left are oxidised. In my experience one or two treatments, each lasting about fifteen hours, with the strong nitric acid and potassium chlorate, followed by deflagration and the process described, sufficed. The residue can be collected as described by Moissan, but the tendency of diamond to

float (as found in check experiments) is in reality a serious difficulty, however much alcohol-spraying of the water surface be carried out. In fact if minute diamonds are present to any appreciable extent, I should think it would be impossible to avoid seeing some of them at this stage of the process. The bulk of the residue seemed to consist of particles of glass in most instances, and was separated by methylene iodide of density 3.34 at 4°.

In the experiments described, no residue that could be collected was ever found, but the treatment with methylene iodide is, I believe, unnecessary, and is certainly an added opportunity for the escape of minute particles of diamond.

Barton (*Nature*, 1905, 72, 397) mentions that some crystals obtained by him supposed to be diamond withstood the action of fused alkali at a red heat.

This test does not appear to have been applied by Moissan, or, if so, he does not mention it either in the "*Four. Electrique*," or in the article on diamond or graphite in the "*Traité de Chimie Minérale*."

It is, however, a very convenient test, for carborundum which is generally present is quickly destroyed by red-hot potassium hydroxide, and, of course, the same remark applies to most of the impurities which have survived to the stage of separation by a dense liquid. In order to make sure that microscopic particles of diamond will survive this treatment, an experiment was made. A diamond was powdered, and the powder passed through a sieve with 100 threads to the inch. Microscopic quantities of this powder were then exposed to the action of potassium hydroxide for five minutes in a small, pure silver ladle at a temperature high enough to cause the edges of the ladle to begin to melt. On washing off the melt, the diamond dust floated on the water after two or three washings as usual, and the fragments were examined under the microscope, when they were found to be unaltered in appearance. The fusion was continued for five or ten minutes. On repeating the experiment with the addition of some crystals of carborundum, five or six times the volume of the diamond fragments, the carborundum disappeared, the diamonds being left as before.

Summary of Information as to the Artificial Production of Diamond.

Moissan claimed to have repeated his classical experiment in one form or another several hundreds of times. He collected diamond and analysed it, and his experiments have been repeated by others with similar results. We may therefore admit that the artificial production of microscopic diamonds is an established fact. In all cases of successful production, carbon had been combined with, or

dissolved in, iron or silver at a high temperature, the mass had cooled as rapidly as experimental requirements, and had been exposed to considerable pressure during the cooling. Some estimate of the quantitative relation of the physical conditions is performed by a detailed consideration of the experiments.

Pressure.—In the form of Moissan's experiment in which a crucible full of a mutual solution, or compound, of iron and carbon at a high temperature was plunged below a cooling liquid, for example, molten lead of greater density than the iron, drops of molten iron containing carbon were separated and solidified as they floated up. Moissan states as the result of his experience that when such drops were small and regular a relatively large yield of diamond was obtained. When the drops showed signs of having burst, no diamond was present. This seems to show that some pressure is necessary. It is not possible to estimate more than the maximum pressure that could have been set up, but this can be done easily. According to Moissan, the more or less homogeneous pasty mixture or compound which exists between iron and carbon at the temperature of an electric furnace separates into two phases, rich in iron and carbon respectively, as cooling occurs, and the increase in volume incident on this separation is greater than the natural decrease attending a lowering of temperature.

When the crucible is plunged below molten lead, the iron phase separates in a more, and the carbon phase in a less, liquid condition than the original paste, and drops of the iron phase detach themselves as soon as the requisite fluidity is reached. The outer layers of the resultant drops must be supposed to acquire the properties of a solid before the separation into two phases is complete in the interior, and hereafter as cooling progresses the compression of the still liquid portion accompanies it, since the relative volume of the inner part tends to increase. Now the pressure which can be set up in this way is clearly limited by the breaking strength of cast iron under tensile stress, and this is approximately known. Moreover, the relation between the tensile stress in the iron and the hydrostatic pressure it can produce is determinate. Prof. Poynting, F.R.S., has kindly deduced the following formula for me from a complete treatment of the problem in *Violle's Cours de Physique*, Vol. I., p. 399.

Let P be the hydrostatic pressure per unit area, T the tensional stress in the shell, supposed uniform, R the radius of the fluid portion, and R' the radius of the sphere. Then

$$P = \left(\frac{2T[R'^3 - R^3]}{R^3 + 2R'^3} \right)$$

The breaking strength of such iron as would separate under the

conditions of the experiment would probably not be more than six or seven tons per square inch, say 1,000 kilograms per square cm. If we then put $R = 1,000$ we can calculate the maximum hydrostatic pressure that can be set up with the following result:

			1,000 kilos./sq. cm.
When $R = 0.5$ cm.	$R = 0.375$ cm.		$P = 0.652$
(2). $R = 0.5$ "	$R = 0.25$ "		$P = 1.40$
(3). $R = 0.5$ "	$R = 0.125$ "		$P = 2.54$
(4). $R = 0.5$ "	$R = 0.05$ "		$P = 4.94$
(5). $R = 0.5$ "	$R = 0.00$ "		$P = 20.00$

In terms of the units employed in the earlier part of this paper, we may say that a breaking strength of ten tons per square inch under tensional stress would probably be an outside figure for the iron, in which case the hydrostatic pressure might possibly rise to twenty tons per square inch. A more likely figure is the one given as case 2, where we have, say, eight or nine tons per square inch pressure, and this is independent of the size of the spheres. In the case of the formation of black diamond in an ingot of silver, a similar increase of volume on setting is shown to occur under the conditions of experiment, but, as the limit of elastic stress in hot silver is not known to me, I can only surmise that the effective pressures were lower than in the case of the iron spheres. Since diamonds were only formed at the centre of the ingot, where the pressure would have been greatest, we may perhaps infer (subject to certain restrictions) that silver can only give just the necessary pressure.

It should be added that in Violle's treatment of the problem, the rigidity and modulus of incompressibility of the metal are treated as independent constants, but it is unlikely that this can be strictly true at really high pressures. The uncertainty introduced in this way in the final formula is probably quite negligible compared with the other uncertainties of the problem.

Temperatures.—Moissan estimates the temperature of his crucible of molten iron at 3000° , when it is withdrawn from the furnace. In the case of iron melted in an arc and allowed to drop into water, the temperature reached could not, have been anything like so high, for the iron would fall off by gravity as soon as it was fairly melted and escape further heating. In the case of silver, the boiling point, which Dr. Harker informs me is about 2100° , would limit the temperature to this point. It is clear that pressure could not have been set up in any case until the temperature was much reduced. The separation of carbon itself appears to take place only after some considerable cooling to a temperature estimated at 1500° . The advantage of a high temperature, if it exists, must therefore lie in the supersaturation of the metal with carbon, or in the formation of a particular compound, which breaks up on cooling, yielding carbon under conditions of

temperature and pressure favourable to the formation of diamond. I ought to add that I do not think it likely that a temperature of 3000° was ever really attained in any of Moissan's experiments. It has also been shown in this paper and by Parsons (*loc. cit.*) that at temperatures of the order of and above 2000° and at high pressures, carbon is converted into well-crystallised graphite when the cooling is not instantaneous. The view harmonising best with the facts as collated would appear to be that the temperatures actually effective at the moment of crystallisation are comparatively low, say of the order of 1500° . At temperatures of 2000° , one would also expect that diamonds, if formed, would be converted into graphite unless the pressure restrained the transformation velocity sufficiently in relation to the rate of cooling to enable some diamond to persist untransformed. This is substantially Roozboom's guess (*Die Heterogenen Gleichgewicht*, 1, 180), together with the acute suggestion that the value of metals as solvents is to be traced to the depression of the carbon crystallisation point by the action of the solvent.

As Roozboom's views on the transformation of carbon receive some support from the experiments described in this paper, and afford besides the most general and concise statement of the problems, they may be briefly restated as follows. Owing to the absence of vapour pressure measurements for both graphite and diamond, it is not possible to plot the vapour-pressure temperature diagram. At ordinary temperatures, the heat of combustion of graphite is slightly greater than that of diamond, but the difference is so small that more accurate work is necessary before the point can be considered settled. The specific heat of diamond is less than that of graphite, so that there would be a tendency as the temperature rises for the heat of transformation (absorption) of diamond to graphite to increase. Graphite being the more stable form at high temperatures, it is unlikely that raising the pressure and temperature sufficiently to melt either diamond or graphite could yield the former, as even if it happened that diamond was the form which crystallised out more easily, it would suffer from a high rate of transformation to graphite. By means of solvents, however, the crystallisation point can be depressed and the transformation velocity of diamond to graphite be reduced, so that if rapid cooling be added it is possible that some diamond may escape conversion.

If we turn to the natural diamonds, we find stones of considerable size, and therefore it is clear either that in Nature excessive rapidity of cooling is unnecessary or that diamond crystallises at an unprecedented rate. The former alternative being more in harmony with general experience in the growth of crystals, I shall adopt it and

examine the consequences. These are that either there must exist in Nature some solvent from which the diamond can crystallise with a very small velocity of conversion to graphite, or that as a result of high pressure the transformation velocity is much reduced, or both effects may exist together. It has not yet been shown that any solvent for carbon other than iron or silver exists having the necessary properties. The work of Friedländer and of Hasslinger, and of Hasslinger and Wolf, does not settle the point, for even if it be admitted that microscopic diamonds were formed in the experiments of these chemists with mixtures of alkali or alkaline-earth silicates and carbon (and no analyses were ever made), still there is no evidence that iron was absent in the mixtures used by Hasslinger and Wolf, and in Friedländer's case (fusion of olivine) it was obviously present. I have pleasure in acknowledging that this was brought to my attention by Mr. Parsons. In Nature, of course, iron is always present, as is shown by the examination of the material with which diamond is associated.

On the whole the facts appear to indicate that what is required for the free formation of diamond is a mixture from which a pure carbon phase can separate at a temperature which is not high enough taking the pressure into consideration for the velocity of transformation to graphite to have any appreciable value. The limits of the temperature interval over which diamond can crystallise without conversion into graphite are probably very near together, whence it seldom happens even in Nature that diamond can be formed rather than graphite. So far as we know the crust of the earth, we can assure ourselves that in fact graphite is an almost indefinitely more usual form than diamond. Moissan made the interesting observation that small quantities of sulphur in the presence of iron increase the yield of diamond. This may be the result of the presence of sulphur helping to depress the crystallisation temperature rather than to reduce the velocity of conversion to graphite, but it may also have what may be described as a direct action on the mode of crystallisation.

There are many cases in which an apparently inert material influences the form, although not the composition, of crystallising substances; for instance, when potassium chlorate separates from solutions containing calcium chloride, it appears in needles instead of plates (Lunge, *Sulphuric Acid and Alkali*, 2nd Ed., 3, 499).

It may happen that the presence of certain substances is advantageous in determining the crystallisation of carbon in the form of diamond, and some support to this view is to be found in the constancy with which iron and alumina appear in the ash of diamonds. Against this, however, Moissan states that he obtained diamonds entirely free from ash, which, however, can only mean that no ash could be perceived in

the small quantity of artificial diamond available. In regard to the effect of pressure, it seems most reasonable, in the light of the experiments recorded in this paper and elsewhere, that pressure may be mainly necessary in enabling the carbon to separate in a sufficiently dense form to be able to crystallise at all. When carbon separates in the laboratory at ordinary pressures and at temperatures which are not too high, the amorphous variety of much lower density than diamond appears, and pressure may be necessary to raise the density of the nascent carbon sufficiently to enable it to crystallise in the denser form. If the view that the formation of diamonds of a size involving slow crystallisation is only possible within very narrow temperature limits be correct, then we must admit that, owing to the larger mass of material involved, natural operations have a great advantage over laboratory experiments. It would be a difficult matter to keep a fusion between 1500° and 1000° , and under a pressure of, say, ten tons per square inch, constant in temperature within one or two degrees for several hours or days, and yet this may be a necessary condition for the formation of diamond. On the above theory, it is clear that the most promising line of research would be to make arrangements to keep a solvent containing carbon under a considerable pressure at the lowest temperature at which carbon could separate, for considerable periods.

CXXIX.—*The Rusting of Iron.*

By WILLIAM AUGUSTUS TILDEN.

THIS is a subject which has been frequently investigated, but that it is still in the controversial stage is shown by the appearance in the Transactions of the Chemical Society within the last three years of two communications from well-known sources, in which the respective authors express contradictory opinions as to the nature of the phenomena. On the one hand, Dunstan, Jowett, and Goulding (Trans., 1905, 87, 1548) uphold the view that the presence of carbonic acid is not a necessary condition, but that contact with oxygen alone is sufficient to produce rusting if the surface of the iron is covered with a film of liquid water. These authors also assume that hydrogen peroxide is formed during the process and that it plays an important part in the production of rust.

On the other hand, Moody (Trans., 1906, 89, 730) maintains the older explanation given long ago by Crace Calvert and Crum Brown, which is based on the opinion that in ordinary atmospheric rusting aerial

carbonic acid is responsible for the initial attack of the iron, rust resulting from the further action of oxygen on the carbonate so formed. Moody, however, goes further in asserting, on the basis of his own experiments, that oxygen alone is unable to attack iron in the presence of water.

Nearly three years ago my attention was drawn to the question, in the first instance chiefly in connexion with the remarkable passivity induced in iron by contact with weak solutions of chromic acid. The statements made by Moody (*loc. cit.*, p. 728) do not accord with my experience. I have preserved specimens of iron partly immersed in a 0.5 per cent. solution of chromium trioxide in contact with ordinary air between two and three years without any sign of rust or of dissolution of the iron, either by change of colour or by the formation of precipitate on adding excess of ammonia.

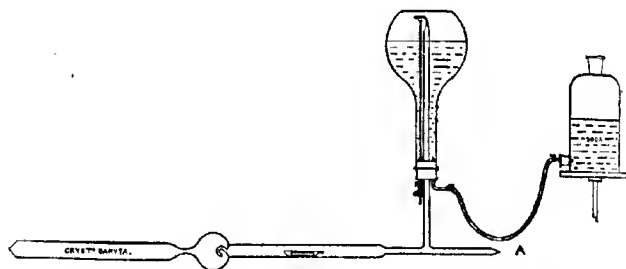
Since these two papers were published in the Transactions of this Society, a paper has appeared in the *Journal of the American Chemical Society* (1907, 29, 1251) by Walker, Cederholm and Bent which contains an account of an investigation of the problem of the corrosion of iron the results of which lead to conclusions with which I am in general agreement. I should have been content to leave the matter to the authors of that paper, but as my experiments have taken a different form, I think they possess some interest as affording contributory evidence toward the main conclusion.

The iron used in most of my experiments was Swedish soft iron in the form of rod $\frac{1}{4}$ inch or about 6 mm. in diameter. It contained no manganese and 0.103 per cent. of carbon. A section kindly made for me by Professor Gowland showed, under a magnification of 3000 diameters, the usual traces of slag disseminated through the mass. The pieces of metal used for experiment were turned bright on the lathe, and, in a few cases, were polished with emery.

I began by a repetition of Moody's experiment (figured p. 722, *loc. cit.*), with the sole difference that instead of placing a single piece of iron in the bend of the tube three pieces were placed in separate bulbs blown on one piece of tube. *A* was a piece of iron partly polished, partly rough-filed, *B* had been heated first in hydrogen to reduce external oxide and then to redness in a vacuum, *C* was a piece of the same iron polished and then immersed in a 1 per cent. solution of chromium trioxide for about twenty-four hours and afterwards well washed. Each piece was protected from contact with the glass by coating the ends with paraffin as advised by Moody. The apparatus included all Moody's arrangements for removing carbon dioxide with addition of a flask containing a 20 per cent. solution of potassium hydroxide through which the entering air bubbled. After drawing air through the whole for five days, water was distilled on to the iron.

On *A* and *B* rusting commenced visibly in about twenty minutes, whilst *C* showed no change. After some time, however, a spot of rust appeared at the end close to the paraffin. About two litres of purified air were drawn through the apparatus each day for two months. The difference between the iron which had been treated with chromic acid and the other specimens was very marked, and even after the lapse of a year and a-half the original spot of rust on the former is the only point attacked, the surface retaining its bright polish.

Other experiments were conducted as follows: (1) a piece of apparatus was constructed as shown in the figure. In order to avoid contact with the glass, the iron, turned to a bright surface on the lathe was placed in a silica boat, inserted in the horizontal tube. The capillary end of the vertical tube being sealed, the apparatus was connected at *A* with the mercury pump and was exhausted as completely as possible, and while in that condition the whole was warmed



by means of a flame applied outside. This operation was continued for some time with the object of removing adherent air before the connexion with the pump was closed by the blow-pipe. The capillary end was then inserted into the flask filled with 20 per cent. solution of sodium hydroxide, oxygen made from pure potassium chlorate was let in, and the whole allowed to remain for three days in the position shown in the figure. On breaking the end of the capillary by means of a wire, oxygen entered the tube containing the iron, and on heating the crystallised baryta, water distilled away and was caused to condense on the iron by the application of a little ice outside. Rusting began in about ten minutes and proceeded rapidly. Another experiment (2) was tried in which greater precautions were taken, the whole glass tube before the introduction of the baryta being made very hot, the iron being shifted from one part of the tube to another as necessary by means of a magnet. After introducing the baryta and sealing up the end of the tube, air free from carbon dioxide was admitted and the

tube evacuated again. This was repeated four times, and finally the tube was sealed off. Water was then distilled from the baryta and allowed to remain in contact with the metal for periods varying from four to ten hours on four successive days. No visible effect was produced. The oxygen was allowed to remain in contact with the sodium hydroxide for a week before admitting it through the capillary into contact with the iron. After the admission of oxygen, rusting soon began, and in twenty minutes was proceeding rapidly.

Many similar experiments were made with similar results. Two only need be mentioned. In the one (3), two exactly similar pieces of iron were used, of which one was wetted with a concentrated solution of sodium hydroxide, the other was supplied with water distilled from baryta. On admitting purified oxygen, the latter rusted rapidly, whilst no action occurred on the former.

In the other experiment (4), a piece of iron, which had been immersed in 1 per cent. chromic acid for two days and then well washed with boiled water, was compared in a similar manner with a piece of the same iron not so treated, but merely turned bright on the lathe. The latter was freely rusted in twenty minutes, whilst the former showed no change until after about two hours, and then and subsequently was attacked only in certain spots, whilst the greater part of the surface remained bright for months.

My attention was then drawn to the experiments of Whitney (*J. Amer. Chem. Soc.*, 1903, 25, 398), which have been adversely criticised by Dunstan, Jowett, and Goulding, although confirmed later by Walker, Cederholm, and Bent (*loc. cit.*). In order to study the effect of water as free as possible from all other substances, the following experiment was made (6).

A piece of iron turned bright was placed in a silica boat enclosed in a glass tube containing baryta and connected with the mercury pump as shown in the figure. The tube was exhausted and heated, a small quantity of water being driven from the baryta in order to assist in the complete removal of air, and finally, the tube being evacuated as completely as possible, its connexion with the pump was sealed. In order to condense water on the iron, the boat had to be cooled by ice while the baryta was gently heated. When the boat was full, the ice was withdrawn and the water gradually evaporated. The operation was repeated daily, except Sundays and holidays. After a few days, a faint discoloration became visible, and it gradually became more marked, the change resulting in the formation of a deep blue film over the whole surface except the scratches left by the tool, which appeared under a lens to have a yellowish colour.

At the end of six months, oxygen, purified as before, was admitted, when the blue film instantly disappeared. Rusting, however, was not

visible until after the lapse of about three-quarters of an hour, but then it spread quickly over the whole of that part of the surface which was wet, and was not restricted to portions of the surface as in previous cases. It appears probable from this that the blue film consists of ferrous hydroxide.

A second experiment of the same kind is proceeding, with similar observed effects.

Inasmuch as these experiments do not permit any settlement of the question whether iron in any form really passes into solution in the water, the experiment originally made by Whitney (*loc. cit.*, p. 398), and repeated by Walker, Cederholm, and Bent (*loc. cit.*, p. 1255), was carried out with such slight modifications as seemed desirable (7). Two Jena flasks, of about 700 c.c. capacity, were thoroughly cleansed by steaming and subsequently boiling distilled water in them for two days. Stoppers were prepared of wide glass tube drawn out for sealing, and were fitted to the necks by means of unvulcanised rubber tubing previously boiled in dilute sodium hydroxide and washed. Water, distilled specially into each flask until about three-fourths full, was kept boiling for about an hour and a half, without condenser, the loss due to evaporation being made up by addition of water boiled separately. The stopper having been inserted, one of the flasks was closed at the blow-pipe. Into the other, boiling continuously, a strip of bright sheet iron, 37—38 sq. cm. of surface, was dropped and the stopper inserted. After boiling another quarter of an hour, this also was sealed and left to cool. After the lapse of a week, both flasks were connected with condensers attached to a water-pump, the pressure reduced, and the water in each flask evaporated without exposure to air so as to avoid the possibility of admission of dust. When concentrated to about 50 c.c., the iron, which was unaltered in appearance, was removed. The liquid was perfectly colourless and clear, but in the course of a few minutes, after admission of air, it became brownish and cloudy. That this was caused by the formation of a precipitate of ferric hydroxide was proved by the application of the usual tests for iron, namely, thiocyanate and ferrocyanide, precautions being taken to avoid mistake arising from possible impurity in the reagents. The water in the blank experiment remained perfectly bright and colourless on exposure to air. This result agrees with that of Walker and his colleagues, and is in harmony with my own experiments already described.

It appears to me, therefore, that iron, in the form of malleable iron, is attacked by water with formation of ferrous hydroxide, which passes into solution if the water is present in sufficient quantity.

But ferrous hydroxide is also the first product of the admission of air or oxygen into contact with iron the surface of which is covered

with water. On several occasions air or oxygen, purified from carbon dioxide, when admitted into a tube containing moist iron, gave rise to the formation of a dark green product which was attracted like other ferrous compounds by the magnet. On further exposure to air this product turns brown, but specimens sealed up have undergone practically no change of appearance in twelve months.

The conclusion is inevitable that the rusting of iron is a process which passes through two stages, of which the first is the production of ferrous hydroxide or, in ordinary air, ferrous carbonate. The initial action is undoubtedly electrolytic, whether water or solution of carbonic acid is concerned. I have ascertained by a special experiment (8) that contact with a less positive metal accelerates the action of water. A piece of iron bound with a ring of platinum wire was sealed up in a tube of the form shown in the figure with the same precautions as in experiment 6, and water from crystallised baryta distilled on to it. The formation of a blue film near to the platinum, and nowhere else, was observed in about a fortnight, whilst without the platinum an equal effect was produced only after the lapse of several months.

That the action in such circumstances is very slow is obviously due partly to polarisation and partly to the slight solubility of ferrous hydroxide, and these conditions together set a limit to the electrolytic action. If anything in the nature of an acid is present, the action is of course greatly promoted. But even in the case of ordinary atmospheric rusting, in which carbonic acid is the electrolyte, the action is facilitated by contact of the iron surface with a depolariser. This is provided in air, whether or not free from carbon dioxide, by the coating of ferric hydroxide which is formed externally. It has been shown that a current will flow through a system consisting of magnetic oxide, water and iron which behaves as the anode (expt. quoted by Walker, *loc. cit.*). A coating of rust, therefore, while wet, is continually suffering reduction on its inner surface, and this action, added to the hydroxylation of the iron, affords an easy explanation of the rapid production of ferrous carbonate or hydroxide, or magnetic oxide.

From what has been said, it would be manifestly futile to attempt to collect the hydrogen evolved during the action of iron on water in the absence of air on account of its extremely small amount. When the process goes on in the presence of air or oxygen, no hydrogen gas would be expected, as it would at once be oxidised into water on the cathodic surface.

Composition of Iron Rust.

Many analyses of iron rust are to be found in chemical literature (compare Mallet, *Brit. Assoc. Report*, 1838, 258; Liversidge, *Nature*, 1892, 45, 424; Grace Calvert, *Chem. News*, 1871, 23, 98).

Dunstan, Jowett and Goulding recall the fact that the composition of rust is somewhat variable, and depends to some extent on the conditions under which rusting has occurred. They also state that it contains a variable proportion of ferrous iron, but they set this fact aside in the endeavour to establish a constant formula, $\text{Fe}_2\text{O}_2(\text{OH})_2$ on the basis of analyses in which the ferrous iron is not distinguished from the ferric.

Moody is right in stating that common air-formed rust frequently contains an appreciable quantity of ferrous carbonate, and that the interior of masses of comparatively fresh rust is commonly black and magnetic. I have had the curiosity to examine one sample of rust which has had exceptional chances of proceeding to the highest degree of oxidation. Some years ago, in company with Professor Thorpe, visited the site of one of the old iron workings on the shore of Loch Maree; we brought away some iron of which analyses were published (Dougal, *Trans.*, 1894, 65, 744; Tilden, *Proc. Birm. Phil. Soc.*, 9, 1). I happen to have kept the whole of the rust from my specimen. The loose external brown portion which separated in the form of dust was sifted through fine gauze and analysed, with the following result:

	I.	II.	Mean.
Fe''	9.15	9.26	9.20 per cent.
Total iron	—	—	62.65

Here is a specimen of a rust which has been exposed to air and rain for some two hundred and fifty years still retaining upwards of 9 per cent. of iron in the ferrous state, or about one-seventh of the total amount of iron present in the substance. There is no carbonate in this specimen, and from the semi-crystalline appearance of much of this rust it appears to consist in part of magnetic oxide, which is known to be very stable. The universal presence of ferrous oxide in rust is significant in regard to the nature of the process, but I feel convinced that no formula can be safely assigned to iron rust in general.

Constitution of Metallic Iron.

The initial stage of rusting being electrolytic in character, a question arises as to the nature of the materials of the couple formed when water or any electrolyte is applied to the surface of the iron. A weak solution of phenolphthalein and ferricyanide, first used as a

reagent by Walker and his colleagues, when applied to the surface of any kind of iron shows in a few minutes areas of opposite polarity. When applied to polished surfaces of grey cast iron, white cast iron, sheet iron and steel, action appears to commence first on grey cast iron and to follow on the other metals in the order mentioned. But different specimens of each react at different rates, and hence it would not be safe at present to infer anything as to their relative rates of rusting. Imbedded graphite, scale and slag are not, apparently, the only substances which promote the action of air and water. The chemical compounds of carbon, silicon, phosphorus and sulphur appear to play a distinct part in the process, being probably negative to iron.

Attention may also be drawn to the work of Richards and Behr on the electromotive force of iron under various conditions (*Carnegie Inst., Washington*, 1906), in which they show that iron quenched in water shows abnormally high electromotive force, and that this increase is due to occluded active hydrogen. As all malleable iron is drawn or rolled in the presence of an atmosphere containing much steam, and cast iron is cast in sand moulds which contain moisture, opportunity is provided for the production of more or less of this active hydrogen within the iron. It is a well known fact that iron commonly contains gas. I have examined at different times many samples of wrought iron and of "pure" iron made by myself, and all, when heated in a vacuum, yield gas containing carbon monoxide and hydrogen (see also recently Belloc, *Compt. rend.*, 1907, 145, 1280, and Boudouard, *Compt. rend.*, 1907, 145, 1283), and usually consisting chiefly of these gases.

Pure iron in the massive form is at present unknown,* and the expression "pure iron," used in the memoirs of Dunstan, Jowett and Goulding, and Walker, Cederholm and Bent, can only mean iron containing very small quantities of foreign elements. The presence of such foreign constituents, although in very various proportions, is sufficient to show that the surface of any piece of iron at present known is not uniform in composition, and consequently that from point to point the surface furnishes in contact with an electrolyte the elements requisite for electrolysis.

This view is further substantiated by the results of my observation of the process of rusting of clean surfaces of iron. The action is often localised in a remarkable way, rapid action occurring along lines or

* My attention has been drawn to a paper by Prof. W. M. Hicks and Mr. L. T. O'Shea, printed in the Commemoration Volume issued by the University of Sheffield, and abstracted in the Brit. Assoc. Report for 1895, in which the authors describe the production of remarkably pure iron by electrodeposition. I have had no opportunity at present of examining this iron.—W. A. T.

restricted areas of the surface, whilst other portions remain untarnished in presence of water and oxygen or air containing carbonic acid for months.

According to Richards and Behr, the active hydrogen contained in iron is not in the form of a compound with iron, a hydride, but they consider that "the most reasonable explanation" of the facts quoted is the hypothesis that the active hydrogen is "dissociated but not ionised." The expression dissociated is used as equivalent to atomic hydrogen without electric charge. On such an assumption this hydrogen could only contribute to the oxidation of the iron indirectly.

As the result of my own experiments, conjointly with those of other chemists already referred to, I consider the following facts established.

1. Commercial iron, liquid water, and oxygen are alone sufficient for the production of rust. Carbonic acid is not necessary, but when present hastens the action.

2. Commercial iron is attacked by pure water in the absence of oxygen and carbon dioxide, the product being, not rust, but ferrous hydroxide.

3. Iron rust always contains ferrous oxide.

4. The process of rusting is due initially to electrolytic action resulting in the production of ferrous hydroxide or carbonate. This may be explained by the presence in all ordinary iron of various components which afford surfaces at different potential in the presence of water, aqueous carbonic acid or other electrolyte.

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CXXX.—*Some Esters of Arsenious Acid.*

By WILLIAM ROBERT LANG, JOHN FRANCIS MACKEY, and
ROSS AITKEN GORTNER.

J. M. CRAFTS (*Bull. Soc. chim.*, 1870, [ii], 14, 99), in referring to the existence of compounds of arsenic with alcohol radicles, pointed out that no esters of arsenious or of arsenic acid had been prepared up to the year 1870, and described a method by which he obtained ethyl, methyl, and amyl arsenates; this consisted in heating the corresponding iodides in sealed tubes at 100° with normal silver arsenate. The esters were purified by washing with ether and distilling under diminished pressure. They are liquids of high boiling

point, above 200° , and suffer partial decomposition if distilled under atmospheric pressure; in the case of the amyl arsenate so much so that he found it impossible to obtain it pure even when distilled in a vacuum. The addition of water to them causes immediate and complete decomposition into arsenic acid and the alcohol. Crafts determined their composition by weighing the precipitated arsenic acid as the magnesium salt and the carbon and hydrogen by combustion, and gave them the formula R_3AsO_4 . For the arsenites of the alkyl radicles he used three methods, a sealed tube being employed: (1) the interaction of arsenious oxide and ethyl silicate at 200° , (2) the interaction of ethyl iodide and silver arsenite at 150° ; and (3) the interaction of arsenic bromide and sodium ethoxide, which last method he considered the best, although in it a secondary reaction between the ester formed and the sodium ethoxide causes a condition of equilibrium to be set up, and no more ester is formed.

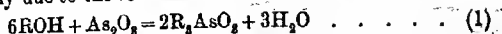
It is to be noted that even if disodium hydrogen arsenite is employed the resulting arsenite is always the trialkyl salt. Crafts states that arsenious oxide and alcohol do not react when heated in a sealed tube, nor does arsenious oxide either with ether alone or with the addition of ethyl acetate, even when in contact for twenty hours.

These esters prepared by Crafts are specified by Auger (*Compt. rend.*, 1902, 134, 238) as the only ones known, and he refers in a later paper (*Compt. rend.*, 1906, 143, 907) to Crafts' inability to obtain any ester by heating the alcohols and oxides of arsenic in a sealed tube. Auger bases his conviction that an ester is produced on the fact that arsenious oxide is volatile in alcohol vapour, although not in water vapour, and concludes that this cannot be accounted for unless there is an ester formed.* Also he succeeded in preparing an ester from glycerol and arsenic oxide, and from ethyl, methyl, isopropyl, isobutyl, and isoamyl alcohols and arsenious oxide. He heated the alcohols with crystalline arsenious oxide for some hours, evidently in a sealed tube, the temperatures quoted are far above the boiling points of the alcohols, and gives 6.5 per cent. as the extreme limit of esterification in the case of methyl alcohol, and 1.2 per cent. in that of ethyl alcohol. Calculating from his figures, the yield of ester for the higher alcohols appears to be 2.62 per cent., 0.25 per cent., 1.00 per cent., and 0.63 per cent. for propyl, isopropyl, isobutyl, and isoamyl alcohols respectively.

So far as can be gathered from the paper, Auger takes no account of the extreme solubility, as we have found, of arsenious oxide in the ester. These small yields and the difficulty found by Crafts in

* We have passed the vapour of methyl alcohol over arsenious oxide heated in a long tube, and the ether obtained differs entirely from methyl arsenite.

obtaining any results from the action of the acid on the alcohol are evidently due to the reversal of the reaction:



Auger states that he removed the water as it was formed by fractional distillation (in the case of *isobutyl* and *isoamyl* esters), or by passing the mixture of alcohol and water vapour over calcium carbide placed in an adapter, thus removing the water and allowing the alcohol to drop back into the flask in which the reaction takes place. An excellent yield, how much is not stated, of propyl, *n*-butyl and *isobutyl* arsenites was thus obtained. Phenol, in the same way, yielded an ester hitherto only prepared by the action of sodium phenoxide on arsenic trichloride.

The nature of the reaction expressed by equation (1) and the properties of the ester clearly show that only by removing the water as it is formed can one expect to get a large yield. Our work has been done in two ways, namely, by heating the mixture in a vessel to which is attached a modified Soxhlet tube and condenser, the Soxhlet containing anhydrous copper sulphate, and by adding this dehydrating agent directly to the mixture. A comparison of the yields obtained is given in the sequel. By these two methods yields of from 14.8 per cent. (cold) to 58.6 per cent. (hot) have been obtained with aliphatic alcohols, and with the phenols as high as 90 per cent. Experiments have also been made, with very encouraging results, on benzyl alcohol and on esters of hydroxy-acids. We hope to show that the use of such a dehydrating agent as copper sulphate in a Soxhlet tube will allow of the preparation of a series of esters from the oxides and possibly sulphides of arsenic, antimony, tin, and perhaps bismuth with compounds containing hydroxyl, where the boiling points of such esters are higher than that of water, as, indeed, is the case with all of these; also with anhydrous copper sulphate in contact with the substances themselves. In many preparations, too, of esters generally and allied products, the formation of water in the reaction produces an equilibrium resulting in a very low yield. It is expected that by removing this water, as is done in the instances described in the present paper, the yields will be greatly increased in many commercial processes.

EXPERIMENTAL.

Heating with Inverted Condenser only.—Weighed quantities of propyl, *isobutyl*, and *isoamyl* alcohols were mixed with excess of arsenious oxide and heated with a direct flame for forty-five minutes in a flask to which a reflux condenser was attached. The clear liquid obtained was poured off from the excess of arsenious oxide and fractionated under diminished pressure. The esters so purified were

analysed and the yield compared with that calculated from equation (1).

Our method of ascertaining the composition of the esters differs from that used by Auger.* The ester was decomposed with water, forming arsenious oxide and liberating the alcohol. The arsenious oxide was dissolved in sodium carbonate and titrated with *N*/10 iodine (a preliminary test having shown that the alcohol did not react with iodine). By this means the quantity of arsenic in the ester was determined.

iso-Amyl Arsenite.—1.4 Grams were decomposed with 10 c.c. of water, sufficient sodium carbonate added to dissolve the arsenious oxide, and the whole diluted to 100 c.c.; 25 c.c. of this required 17 c.c. of standard iodine for oxidation, corresponding with 22.4 per cent. of arsenic. In 50 grams of the ester, the alcohol was determined and found to weigh 39 grams, or 78 per cent. *iso*Butyl and propyl arsenites were also analysed in a similar way :

Ester.	Per cent. As found.	Per cent. As calculated as $(RO)_3 As$.
Methyl.....	44.5	44.6
Ethyl.....	—	—
Propyl.....	29.6	29.7
<i>iso</i> Butyl.....	25.7	25.5
Amyl.....	22.2	22.3
<i>iso</i> Amyl.....	22.4	22.3

Expressing these as salts of arsenious acid, the formulæ become $(C_4H_{11})_3AsO_3$, $(C_4H_9)_3AsO_3$, and $(C_3H_7)_3AsO_3$.

Propyl arsenite is a yellow, mobile liquid boiling at 216° and decomposing very readily on addition of water.

*iso*Butyl arsenite is a deep yellow, mobile liquid of specific gravity 1.069; it decomposes rapidly in presence of water into *isobutyl* alcohol and arsenious oxide; under 760 mm. pressure it decomposes at 242° , and boils at 157° under 30 mm. pressure.

*iso*Amyl arsenite is a yellow liquid of specific gravity 1.050; it boils at 185° under 30 mm. pressure, and under atmospheric pressure it decomposes at 284° ; in the presence of water, it decomposes into *iso*amyl alcohol and arsenious oxide.

Heating with Soxhlet Attachment and Anhydrous Copper Sulphate.—To eliminate the water as it is formed and so increase the yield of ester, the conditions of the experiments were modified. One hundred and sixty grams of *iso*amyl alcohol were added to 70 grams of

* Auger determined the amount of arsenic in the cooled liquid obtained (a mixture of the ester and alcohol) by means of iodine. The difference between this and the amount of arsenious oxide that would dissolve in the same quantity of alcohol in the cold was taken as representing the amount of ester formed (*Compt. rend.*, 1906, 143, 998). No account was taken of the solubility of arsenious oxide in the esters themselves.

arsenious oxide in a 300 c.c. flask. An ordinary Soxhlet tube was connected with the flask, and a condenser, fitted with a calcium chloride tube, was attached to the Soxhlet, which contained a large filter paper filled with anhydrous copper sulphate. The liquid in the flask was heated to boiling, and the water formed was absorbed by the anhydrous copper sulphate, which turned blue as soon as the first drops of condensed liquid fell on it. Heating was stopped after forty-five minutes, when small rings of a compound of high boiling point began to form on the sides of the flask; after cooling, the clear product was filtered and fractionated under diminished pressure. 110.25 grams of ester were obtained, being a yield of 58.6 per cent. as compared with 13.22 per cent. obtained without the use of a dehydrating agent.

In similar experiments with *isobutyl* and *propyl* alcohols, yields of 56.25 per cent. and 56.75 per cent. respectively were obtained, as compared with 11.09 and 8.79 per cent. when no dehydrating agent was employed.

Use of Dehydrating Agent in the Cold.—The esterification of these three alcohols by arsenious oxide can be carried out even in the cold if a dehydrating agent is used; 120 grams of the alcohol were shaken in a stoppered bottle at room temperature with 60 grams of arsenious oxide and 70 grams of anhydrous copper sulphate for three days. The following yields were obtained: *isoamyl* arsenite, 17.2 per cent.; *isobutyl* arsenite, 15.8 per cent.; *propyl* arsenite, 14.8 per cent.

The following table indicates the comparative yields (per cent.) by different methods:

Ester.	Auger (in sealed tube).	Reflux condenser.	With anhydrous copper sulphate:	
			in Soxhlet.	in the cold.
Methyl	6.5	—	33.8*	—
Ethyl	1.2	—	4.5*	—
Propyl	2.62	8.79	56.75	14.8
<i>isoButyl</i>	0.25	11.09	56.25	15.8
Trimethylcarbinol	—	—	54.27	—
Amyl	1.00	—	54.00	—
<i>isoAmyl</i>	0.63	13.22	58.62	17.2

* The Soxhlet was not used, but the anhydrous copper sulphate was placed with the alcohol and arsenious oxide in a flask fitted with a reflux condenser.

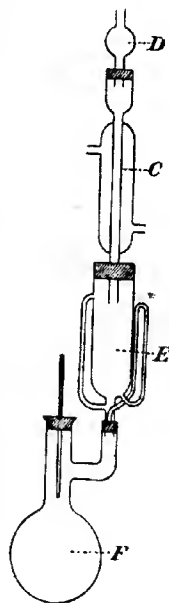
A probable explanation of the low yield in the case of the ethyl arsenite lies in the fact that ethyl alcohol itself has a strong affinity for water which, for small quantities of water present, cannot be overcome by the anhydrous copper sulphate. This is readily shown by adding a drop of water to 5 c.c. of ethyl alcohol in which a little anhydrous copper sulphate has been placed. The copper sulphate is apparently not affected, whilst in the case of the higher alcohols a blue colour appears almost instantly, showing the hydration of the

copper sulphate. Methyl alcohol does not respond to this test as readily as do the higher alcohols, but it responds more readily than does ethyl alcohol. The yield in each case, using the copper sulphate, probably bears a direct relation to the respective affinities of the alcohol and of the copper sulphate for the water of the reaction. If a substance could be used which had a greater dehydrating power and at the same time was insoluble in alcohol, a higher yield would doubtless be obtained. Calcium carbide (Auger, *Compt. rend.*, 1906, 143, 908) is not such a material: we have compared the yields obtained by replacing the anhydrous copper sulphate in the Soxhlet with fresh calcium carbide, using various alcohols, and the highest yield was in the case of *isoamyl* alcohol where 40.2 per cent. of ester was obtained after two hours' heating.

Esters obtained with Phenol and its Homologues.

For the esterification of these with arsenious oxide a side-necked flask was used the neck of which was bent upwards and attached to the Soxhlet, leaving the mouth of the flask free to receive a thermometer (see figure).

Phenyl Arsenite.—Weighed quantities of phenol (140 grams) and arsenious oxide (80 grams) were heated together, and in all cases it was observed that the reaction began at 100°, the mixture boiling violently at that temperature. The thermometer gradually rose to 133°, when a thick cloud formed in the flask. The temperature remained constant at that point for a few minutes and then gradually rose to a maximum, where it was kept for about five minutes: the heating was then stopped and the contents of the flask allowed to cool. The mixture of phenol, ester, and arsenious oxide, the latter of which is very soluble in the ester, was shaken with benzene, causing the precipitation of the arsenious oxide dissolved in the ester. The mixture was then filtered and the benzene solution of the ester fractionated under diminished pressure. The benzene distilled at 20°, the phenol at 69°, and the ester at 305°. The ester, purified by redistillation, weighed 105 grams, representing a yield of 60 per cent. *Phenyl arsenite* is a deep yellow, viscous liquid with a specific gravity of 1.59; it freezes at 31°, and boils at 305° under a pressure of 30 mm. It dissolves readily in methyl alcohol, benzene, ethyl acetate, or chloroform, and decomposes on addition of water, but not



so readily as the fatty arsenites. It was found on analysis to correspond with the formula $(C_6H_5O)_3As$, or $(C_6H_5)_3AsO_3$.

o-, *m*-, and *p*-Tolyl Arsenites.—One hundred grams of each of the cresols were heated with arsenious oxide for thirty minutes in the apparatus previously described, the arsenious oxide being separated by benzene. The liquid was then fractionated, and the esters, after having been purified and analysed as in the case of the phenyl arsenite, were found to correspond with the formulæ $(C_6H_4Me)_3As$, or $(C_6H_4Me)_3AsO_3$.

Naphthyl Arsenite.—One hundred grams of naphthol were heated with 30 grams of arsenious oxide for thirty minutes and the arsenious oxide in the ester separated by means of benzene. As yet, however, the pure ester has not been isolated.

Benzyl Arsenite.—One hundred grams of benzyl alcohol were heated with 35 grams of arsenious oxide for thirty minutes. The maximum temperature was 240° . The clear liquid was decanted and 75 c.c. of benzene added, the arsenious oxide collected, and the filtrate fractionated under 30 mm. pressure. The *benzyl arsenite* distilled at 285° , suffering partial decomposition. Although in the case of the fatty alcohols a drying agent in the Soxhlet was essential to absorb the water formed and to allow only the alcohols themselves to drop into the mixture, no such device was necessary with the phenols, as practically no phenol or ester ever found its way further than the side tube of the Soxhlet. The water formed remained in this apparatus, there being never sufficient volume of liquid produced to cause the syphon attachment to come into play.

To ascertain if it was possible to obtain these esters without the removal of the water formed during the reaction, the same quantities of phenol, benzyl alcohol, *o*-, *m*-, and *p*-cresol respectively, as were used in the previous experiments, were heated with arsenious oxide in a flask fitted with a reflux condenser only, but in no case was any arsenite formed in quantities sufficient to enable it to be isolated.

Method of Analysis for Esters of Phenol and its Homologues.—To determine the composition of the esters, it was found necessary to distil them several times in order to remove all traces of arsenious oxide which is readily soluble in them, in some cases to the extent of 30 per cent. About 3 grams of the ester were decomposed by 5 c.c. of water and 10 c.c. of potassium hydroxide (containing 700 grams of potassium hydroxide per litre), and the whole diluted to 500 c.c. Two samples of 10 c.c. each were taken for analysis; to one sample standard iodine was added in excess, shown by the formation of a precipitate of tri-iodophenol and the appearance of a clear yellow solution, the temperature being kept at 65° . The mixture was then cooled, acidified with sulphuric acid, and diluted to 500 c.c. with

water. The excess of iodine in 100 c.c. of this was titrated against standard thiosulphate, using starch as indicator. The quantity of thiosulphate necessary, multiplied by five, represents the quantity of iodine used. This quantity, subtracted from the original amount of iodine added, gave the amount necessary to change both the phenol to tri-iodophenol and the arsenious oxide to arsenic oxide. To determine the quantity of arsenious oxide present in the ester, an excess of standard potassium dichromate was added to the second sample and this excess was determined with standard ferrous sulphate. The ratio between the dichromate and iodine being known, the number of c.c. of iodine equivalent to the amount of dichromate used was found and subtracted from the total iodine obtained in the previous determination, the difference being the amount combined with the phenol. From these data the relative quantities of arsenious oxide and phenol, formed by decomposing the ester, were obtained, and the composition of the ester thus determined.

To test the accuracy of this method, estimations were made with weighed quantities of (a) phenol, (b) arsenious oxide, (c) a mixture of these.

(a) To 0.8826 gram of phenol, 5 c.c. of potassium hydroxide (700 grams per litre) were added and the whole diluted to 250 c.c. . (1)
Ten c.c. of this solution were found to be equivalent to 25.75 c.c. of standard iodine.

(b) To 0.5 gram of arsenious oxide, 5 c.c. of the same potassium hydroxide were added and diluted to 250 c.c. (2)

Ten c.c. of this solution were found to be equivalent to 6.5 c.c. of standard iodine.

(c) To 10 c.c. of solution (1), 10 c.c. of solution (2) were added and found to require 32.30 c.c. of standard iodine.

Thus 10 c.c. of solution (1) required 25.75 c.c. of iodine, and 10 c.c. of solution (2) required 6.50 c.c. of iodine; in all 32.25 c.c. as compared with 32.30 c.c. when mixed, a difference which is well within the limits of experimental error.

In order to see if arsenious oxide can be determined accurately in the presence of phenol by means of dichromate, experiments similar to those made with iodine were carried out with it. Ten c.c. of solution (2) required 6.07 c.c. of dichromate, a mixture of 10 c.c. of (2) with 10 c.c. of (1) required 6.09 c.c. of dichromate, or an error of less than 0.3 per cent.

Properties of the Arsenites prepared from Phenol and its Homologues.

	Phenyl arsenite.	Benzyl arsenite.	<i>o</i> -Tolyl arsenite.	<i>m</i> -Tolyl arsenite.	<i>p</i> -Tolyl arsenite.
Yield (per cent.)					
(a) with Soxhlet	60	100	96	94	95
(b) without Soxhlet	nil	nil	nil	nil	nil
Specific gravity	1.59	1.43	—	1.45	1.46
Refractive index *	—	1.572	—	—	—
Boiling point † under 30 mm. .	305°	255°	—	346°	—
Freezing point	-31°	-36°	—	—	—
Colour	yellow	blue	dark brown	dark brown	brown

* The blanks indicate that the refractive index is greater than 1.62098, the limit of the prism used.

† Where the boiling point is not given it is above 360°.

All these esters are soluble in methyl and ethyl alcohols, ether, benzene, ethyl acetate, or chloroform, and are decomposed at once by water.

This method of esterification is being carried out with arsenious oxide and the dihydric and trihydric phenols, but the quantitative results are not yet ready. A successful attempt has also been made to form similar esters with hydroxy-acids, methyl salicylate being heated with arsenious oxide. The products of the reaction, namely, water and an oil, were driven up into the Soxhlet where the latter decomposed, liberating arsenious oxide. The oil boils at about the same temperature as the methyl salicylate and has an almost unbearable odour. When the dehydrating agent is used in the Soxhlet it is expected the new ester will readily be separated.

Experiments have also been tried with arsenious sulphide in place of the oxide and a small yield of an ester obtained, presumably of the composition R_3AsS_3 , but the upper portions of the flask and the condenser became coated with the orange-coloured arsenious sulphide, showing that decomposition had occurred. The work is being continued.

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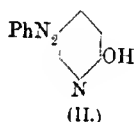
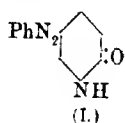
CXXXI.—*Benzeneazo-2-pyridone.*

By WILLIAM HOBSON MILLS and SYBIL T. WIDDOWS.

THE 3-substituted derivatives of pyridine show a far-reaching analogy to the corresponding compounds of benzene. This is, however, not the case with the 2-derivatives; in these the substituent radicle appears to become deprived, in many respects, of its aromatic character through the closer influence of the nitrogen.

This is especially noticeable in the case of 2-aminopyridine, which, unlike the 3-derivative, is incapable of yielding diazo-solutions in the usual manner (Marckwald, *Ber.*, 1894, 27, 1318). 2-Chloropyridine, again, shows little of the chemical indifference characteristic of chlorobenzene (Friedländer and Ostermaier, *Ber.*, 1882, 15, 335), the chlorine atom being readily eliminated under the influence of hydriodic acid, sodium ethoxide, ammonia, amines, &c. Finally, 2-pyridone differs in many respects from phenol, giving, for instance, neither a phenolic coloration with ferric chloride (v. Pechmann and Baltzer, *Ber.*, 1891, 24, 3146), a nitroso-derivative, nor Lieberman's phenol reaction (v. Pechmann and Baltzer, *loc. cit.*), and being also incapable of acetylation.

It was therefore of some interest to us to find that, in spite of such facts, when an alkaline solution of 2-pyridone is brought together with benzenediazonium chloride, coupling takes place with the formation of a product which we have been able to show is 5-benzeneazo-2-pyridone (I)



[or the tautomeric hydroxylic form (II)].

The coupling, however, takes place with much smaller velocity than is the case with phenol, and in spite of the formal analogy there is little resemblance in external features between this reaction and the coupling of phenol. There is no rapid precipitation of the dyestuff, although the reaction is carried out in presence of a minimum of alkali, and the velocity of coupling being little greater than that of the spontaneous decomposition of the alkaline diazo-solution, the presence of the bisbenzeneazophenol, &c., together with tarry matter proceeding from this decomposition, renders the purification of the product difficult and considerably affects the yield.

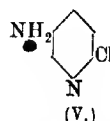
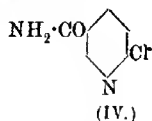
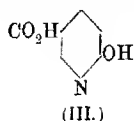
As with phenols of the benzene series, excess of alkali retards coupling, and the presence of even traces of acid prevents it altogether.

5-Benzeneazo-2-pyridone is a bright yellow substance, and is thus much paler in colour than benzeneazophenol. It dissolves in sodium hydroxide, forming a sodium salt sparingly soluble in excess of the alkali, and acts as a weak dye.

With regard to its constitution, although it appeared most probable that the benzeneazo-complex would enter the para-position relatively to the hydroxyl group, this could scarcely be taken for granted. In view of the exceptional character of 2-pyridone, it might be regarded as not

altogether impossible that, as is the case with the pyrazolones and the aliphatic enolic substances, the benzeneazo-complex should become attached to the carbon atom adjacent to that attached to the oxygen.

The proof that the product, however, actually has the constitution assigned to it was obtained by showing its identity with the substance resulting from the substitution of a benzeneazo-group for carboxyl in 6-hydroxynicotinic acid (III) (Königs and Geigy, *Ber.*, 1883, 16, 2158; v. Pechmann and Welsh, *Ber.*, 1884, 17, 2391).



The transformation was effected by the following series of reactions. The acid was first converted as described by v. Pechmann and Welsh (*loc. cit.*) into 6-chloronicotinic chloride, and this, on treatment with ammonia in benzene solution, gave rise to the corresponding amide (IV). (The object of this replacement of the hydroxyl group by chlorine was to give the molecule the requisite stability to withstand the oxidising influences to which it was to be subjected in the two following reactions.) The chloroamide was next converted by sodium hypobromite into 2-chloro-5-aminopyridine (V), which crystallises readily, and, like 3-aminopyridine, yields normal diazo-solutions. This chloro-base was then treated with nitrosobenzene in glacial acetic acid solution and thereby transformed into 2-chloro-5-benzeneazopyridine.

With the aid of this substance it was possible doubly to establish the constitution of the hydroxyazo-compound. For on the one hand an identical chloroazo-compound was obtained by replacing the hydroxy-group by chlorine by means of phosphorous pentachloride, and on the other hand, the reverse reaction, namely, the replacement of the chlorine in this substance by hydroxyl by treatment with sodium methoxide, gave rise to a hydroxyazo-compound identical in all respects with that derived from the coupling of benzenediazonium chloride with alkaline 2-pyridone.

The behaviour of an alkaline solution of 3-hydroxypyridine towards benzenediazonium chloride has also been examined. In this case, coupling takes place with much greater rapidity. It is, however, associated with the production of much tarry matter, and the yield leaves much to be desired. *Benzeneazo-3-hydroxypyridine* is a substance of reddish-brown colour, very different from the bright yellow of the 2-hydroxy-compound. Indeed, the difference in colour is so marked as at first sight to seem to afford evidence that the two substances differ in type, that the latter is a pyridone (formula I, p. 1373) and not a

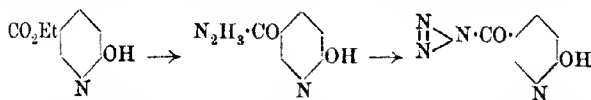
hydroxy-compound; since, however, its sodium salt is similarly pale in colour, it would appear that little stress is to be laid on this point.

We have also studied the behaviour of 5-benzeneazo-2-pyridone on reduction, since it seemed a question of some interest whether the presence of a hydroxyl-group in the para-position with respect to a benzeneazo-complex would, in a pyridine compound, as in the case of benzene and naphthalene derivatives, lead to the fission of the latter by mild reducing agents which otherwise give rise only to a hydrazo-compound.

When treated with sodium hyposulphite, the colour of the azo-compound is discharged (although not quite so rapidly as in the case of benzeneazophenol under the same conditions), and the solution then contains aniline and 5-amino-2-pyridone, and, although experimental difficulties prevented the determination of how nearly quantitatively the reaction proceeds, we have found no indication of the presence of a hydrazo-compound. The properties of the aminopyridone were unfortunately such as to render its extraction a matter of difficulty, and it was found desirable first to effect its preparation in some other manner.

This was partly accomplished in two ways. In the first, the carboxyl group in hydroxynicotinic acid was replaced by the amino-group according to Curtius's method (*Ber.*, 1894, 27, 778), which, on account of the oxidisability of the product, seemed in this case particularly applicable.

The ester of the acid was converted by means of hydrazine hydrate into the *hydrazide*, which was then transformed into the *azide* by nitrous acid.



On boiling with water, the azide undergoes the transformation into the corresponding substituted carbamide, a reaction which Curtius (*loc. cit.*) has shown to be characteristic of this class of compounds.

Finally, this carbamide, on hydrolysis with concentrated hydrochloric acid under pressure, gives rise to 5-amino-2-pyridone hydrochloride. The alternative method of formation of the base consisted in replacing the chlorine in 2-chloro-5-amino-pyridine (V, p. 1374) by hydroxyl. This was readily effected by sodium methoxide, the reaction resulting here, as in the case of the chlorazo compound, in a direct substitution of chlorine by hydroxyl, the methoxy-derivative not appearing.*

* This action of sodium methoxide is somewhat remarkable, and is possibly connected with the interesting transformations of 2- and 4-methoxypyridines (Haitinger

It is noteworthy, however, that the chlorine in this chloroaminopyridine is distinctly less reactive than that in the chloroazo-compound. Whereas the latter reacts practically quantitatively with sodium methoxide at 100°, the former remains almost unaltered under these conditions, and is only readily attacked at a temperature some 20–30° higher. This is apparently analogous to the fact observed by Marckwald (*Ber.*, 1894, 27, 1317), that the presence of a negative (carboxyl) group in the 3-position in a pyridine derivative facilitates the replacement of an ortho- or para-chlorine atom by ammonia, the benzeneazo-group being known to have the character of a negative substituent (Hantzsch and Farmer, *Ber.*, 1899, 32, 3093, 3095; Farmer, *Trans.*, 1901, 79, 870).

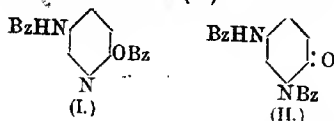
By these methods, the hydrochloride of the aminopyridone is obtained as a syrup crystallising after a short interval. Analysis, however, showed it to be impure, and no satisfactory means of recrystallising it was discovered. On liberating the base with sodium hydrogen carbonate, a solution was obtained possessing strong reducing powers, and very rapidly darkening in the air, from which little crystallisable could be extracted.

As it became clear that the isolation of the pure base would require the expenditure of a considerable amount of material, we desisted from further attempts, especially as the possession of the base itself was not essential to the end we had in view.

On shaking the crude substance obtained by either method with benzoyl chloride in sodium hydrogen carbonate or in dilute alkaline solution, a white crystalline *benzoylaminopyridyl benzoate* is formed; and when the solution obtained by reduction of the hydroxyazo-compound is rendered alkaline, and similarly treated with benzoyl chloride (after having been freed as far as possible from aniline), this same benzoyl derivative is precipitated.

and Lieben, *Monatsh.*, 1895, 6, 322; H. Meyer, *Monatsh.*, 1907, 28, 33). The sodium methoxide employed was prepared from anhydrous methyl alcohol, and although, no doubt, traces of water were absorbed during the subsequent manipulation, the minute proportion of sodium hydroxide thereby produced can hardly be the cause of the production of the hydroxy- in place of the methoxy-derivative, seeing that, in the analogous case of 2-chloroquinoline-3-carboxylic acid, the replacement of chlorine by ethoxyl can be brought about by boiling with alcoholic potash (Friedländer and Göhring, *Ber.*, 1884, 17, 469). Temperature plays an important part in determining the course of the reaction: we find that when 2-chloroquinoline-3-carboxylic acid is treated with sodium methoxide at 100°, there is produced, as described by H. Meyer (*Monatsh.*, 1907, 28, 47), the methoxy-acid, together with a trace of the hydroxy-acid, but if the reaction is carried out at 130–140°, the latter is the sole product. Moreover, the observation of H. Meyer (*loc. cit.*) that 2-methoxypyridine-5-carboxylic acid gives rise to the hydroxy-acid on heating to 260° is also noteworthy in this connexion.

As regards its constitution, we have not failed to consider the possibility of the pyridone formula (II):



but since the same compound is formed on benzylation in pyridine solution (under which conditions *O*-derivatives are preferably formed, Auwers, *Ber.*, 1904, 37, 3899 *), the alternative formulation (I) seems the more probable.

The fact that on treatment with alkalis the second benzoyl group behaves like that in phenyl benzoate, and differs from that in benzanilide in being comparatively readily eliminated, seems also to support this view; it is possible, however, that the presence of the pyridone oxygen in a compound of formula II might facilitate the removal of the adjacent *N*-benzoyl group.

EXPERIMENTAL.

5-Benzeneazo-2-pyridone, \dagger $C_6H_5 \cdot N_2 \cdot C_6H_4ON$.

A solution of benzenediazonium chloride is exactly neutralised with normal sodium hydroxide, and added to a molecular proportion of 2-pyridone \ddagger dissolved in the equivalent volume of ice-cold normal sodium hydroxide.

The mixture becomes pale yellowish-brown, and slowly darkens; at the same time a slight turbidity and gas evolution, such as are always observed when an alkaline diazo-solution is allowed to stand, gradually make their appearance. After remaining for ten minutes at 0° , the liquid is filtered and the clear filtrate acidified with dilute acetic acid, when the pale yellow, flocculent azo-compound is precipitated. After a short time this is collected, dissolved in dilute alkali, reprecipitated by carbon dioxide and dried. After several recrystallisations from toluene, the pure substance separates in long, fine bright yellow needles melting at $210\text{--}212^\circ$. In this way, from 2 grams of 2-pyridone about 1 gram of the crude product is obtained. If the mixture is allowed to stand for a longer time before acidification, the weight of crude material is greater, but the loss entailed in the purification is then heavier and the yield of pure product less:

* These results may probably be taken to hold good also in the case of tautomeric substances.

\ddagger This nomenclature is employed for convenience only. The question whether this substance is a pyridone or a hydroxypyridine derivative is left quite open.

\dagger This was prepared by distilling hydroxynicotinic acid in a vacuum (v. Pechmann and Baltzer, *Ber.*, 1891, 24, 3145).

0.1132 gave 0.2731 CO_2 and 0.0482 H_2O . $\text{C} = 65.8$; $\text{H} = 4.7$.

0.1341 „ 0.3288 CO_2 „ 0.0568 H_2O . $\text{C} = 66.8$; $\text{H} = 4.7$.

0.1462 „ 27.3 c.c. N_2 at 18.5° and 742 mm. $\text{N} = 21.0$.

$\text{C}_{11}\text{H}_9\text{ON}_3$ requires $\text{C} = 66.3$; $\text{H} = 4.5$; $\text{N} = 21.1$ per cent.

Coupling does not appear to take place except in the presence of free alkali. The pyridone and diazonium salt seem quite indifferent to one another in the presence of sodium acetate or sodium hydrogen carbonate. Further, the retarding effect of excess of alkali, investigated by Goldschmidt and his pupils (*Ber.*, 1897, 30, 670; *Ber.*, 1900, 33, 893) as regards the phenols of the benzene and naphthalene series, is also apparent in this case, the yield of hydroxyazo-compound being less in the presence of a greater quantity of sodium hydroxide.

5-Benzeneazo-2-pyridone is sparingly soluble in water or ether, moderately so in chloroform, acetone, or benzene, and readily so in alcohol and glacial acetic acid. It is best recrystallised from toluene. Its solution in concentrated hydrochloric acid is a deep reddish-orange. When added to a 12 per cent. solution of sodium hydroxide, it partly dissolves, forming a zone of coloured solution in which in a few minutes an abundant crystallisation of the sparingly soluble yellow sodium salt occurs.

5-Benzeneazo-2-pyridone dyes wool a pale yellow colour which is distinctly weaker than that produced by an equivalent quantity of benzeneazophenol.

An experiment was made to see whether the same product would be formed by the action of diazo solutions on hydroxynicotinic acid with replacement of the carboxyl group in analogy to the formation of benzeneazophenol from *p*-hydroxybenzoic acid. The reaction was found to take place very slowly, and after the mixture had remained overnight in an ice-chest, only a small amount of a substance was obtained, which, however, after three recrystallisations from toluene, melted at $208-210^\circ$, and was therefore presumably the benzeneazo-pyridone, although still in a somewhat impure condition.

Benzeneazo-3-hydroxypyridine, $\text{C}_6\text{H}_5\cdot\text{N}_2\cdot\text{C}_5\text{H}_6\cdot\text{N}\cdot\text{OH}$.

A solution of benzenediazonium chloride is added to a dilute ice-cold solution of the hydroxypyridine in so much sodium hydroxide as to leave in the solution after mixture an amount of alkali equivalent to the hydroxypyridine. The azo-compound is precipitated at once, accompanied by much yellowish-brown, tarry matter. After ten minutes this is filtered off, and a further quantity is obtained by acidifying the filtrate with acetic acid.

The tarry product is freed from oily matter by drying on a porous tile, and is then crystallised repeatedly from toluene, and, finally,

from dilute alcohol, from which it separates in reddish-brown plates melting at $167-169^{\circ}$:

0.1448 gave 0.3504 CO_2 and 0.0632 H_2O . $\text{C} = 66$; $\text{H} = 4.8$.

0.1561 " 26.8 c.c. N_2 at 10° and 769 mm. $\text{N} = 20.8$.

$\text{C}_{11}\text{H}_5\text{ON}_3$ requires $\text{C} = 66.3$; $\text{H} = 4.5$; $\text{N} = 21.1$ per cent.

The substance is readily soluble in ether or alcohol, but sparingly so in toluene or chloroform. Its solution in sodium hydroxide is deep reddish-brown.

Synthesis of 5-Benzeneazo-2-pyridone.

6-Chloronicotinamide, $\text{NH}_2 \cdot \text{CO} \cdot \text{C}_5\text{H}_3\text{NCl}$.

Well dried hydroxynicotinic acid is moistened with freshly distilled phosphoryl chloride and heated in an oil-bath to 100° . Three parts of phosphorus pentachloride are gradually added, and the temperature then allowed to rise during ten minutes to 120° . The phosphoryl chloride is distilled in a vacuum, the gunmy residue of chloronicotinic chloride dissolved in benzene, and dry ammonia led into the well-cooled solution for from one-half to three-quarters of an hour. A white solid separates consisting of a mixture of the amide with ammonium chloride. It is collected, and the ammonium chloride removed by a single crystallisation from water, from which the amide separates in long white needles melting at $210-211^{\circ}$. The yield is nearly quantitative:

0.1327 gave 0.1225 AgCl . $\text{Cl} = 22.8$.

$\text{C}_5\text{H}_3\text{ON}_2\text{Cl}$ requires $\text{Cl} = 22.7$ per cent.

2-Chloro-5-aminopyridine, $\text{NH}_2 \cdot \text{C}_5\text{H}_3\text{NCl}$.

Five grams of chloronicotinamide are finely powdered and dissolved in a hypobromite solution prepared from 5 grams of bromine and a solution of 26.7 grams of potassium hydroxide in 480 grams of water. After shaking the mixture for an hour, it is heated at 70° until the hypobromite has disappeared (as shown by the fact that no bromine is liberated on acidification with acetic acid). The solution is then cooled, acidified with acetic acid, rendered alkaline,* and extracted at least nine or ten times with ether. The ethereal solution leaves on evaporation a brown, crystalline mass, which is best purified by recrystallisation from hot water, followed by several recrystallisations from toluene. It melts at $82-83.5^{\circ}$. The yield is about 50 per cent. of the theoretical:

* Without this previous acidification, no amine is obtained on extraction with ether. If the hypobromite solution is acidified before heating to 70° , a crystalline substance, not further examined, but presumably the bromamide, separates.

0.1143 gave 21.5 c.c. N_2 at 18° and 753 mm. $N = 21.5$.

0.1001 „ 0.1116 AgCl. $Cl = 27.56$.

$C_8H_5N_3Cl$ requires $N = 21.8$; $Cl = 27.62$ per cent.

2-Chloro-5-aminopyridine dissolves very readily in alcohol or ether. It is only moderately soluble in cold water or benzene. It crystallises well from toluene or xylene. A solution of the base in dilute hydrochloric acid treated with nitrous acid gave a diazo-solution which coupled with an alkaline solution of β -naphthol, forming a red azo-dye.

2-Chloro-5-benzeneazopyridine, $C_6H_5 \cdot N_2 \cdot C_5H_3NCl$.

2-Chloro-5-aminopyridine is dissolved in a little glacial acetic acid and added to a nearly saturated solution of nitrosobenzene in the same solvent. The vessel containing the mixture is allowed to stand for twelve to twenty-four hours in cold water, when a mass of crystals will have separated. From the mother liquor a second less pure crop can be obtained by the cautious addition of water. Three grams of the base gave about 2.6 grams of the condensation product. The substance was purified by several crystallisations from alcohol, from which it separates in small, flattened, orange-coloured prisms melting at $108-109^\circ$:

0.1268 gave 21.8 c.c. N_2 at 16.5° and 746 mm. $N = 19.6$.

0.1202 „ 0.0806 AgCl. $Cl = 16.57$.

$C_{11}H_5N_3Cl$ requires $N = 19.3$; $Cl = 16.32$ per cent.

2-Chloro-5-benzeneazopyridine is volatile in steam, and has a characteristic sweet odour. It is sparingly soluble in cold water, ether, cold alcohol or acetone, but readily so in hot water or benzene.

Preparation of 2-chloro-5-benzeneazopyridine from Benzeneazo-2-pyridone.

Benzeneazo-2-pyridone is moistened with freshly distilled phosphoryl chloride, heated in an oil-bath at 115° , and an equal weight of phosphorus pentachloride gradually added. After ten minutes' further heating, the phosphoryl chloride is distilled in a vacuum and the residue purified by crystallisation from alcohol. It agreed in appearance, odour and solubility with the substance obtained from chloroaminopyridine and nitrosobenzene. It melted at $108-109^\circ$, and the mixture of the two products melted sharply at this temperature. They are therefore identical.

Conversion of 2-Chloro-5-benzeneazopyridine into 5-benzeneazo-2-pyridone.

2-Chloro-5-benzeneazopyridine was heated with a 10 per cent. solution of sodium in anhydrous methyl alcohol for twenty-four hours or more in sealed tubes in a boiling-water bath.

The excess of sodium methoxide was then neutralised with dilute sulphuric acid, the sodium sulphate filtered off, the alcohol evaporated and the product extracted from the neutralised residue with ether, in which, however, it is not very soluble. The ethereal residue was crystallised from toluene, and there was thus obtained a bright yellow crystalline substance melting at the same temperature ($210-212^{\circ}$) as the product of coupling 2-pyridone with benzenediazonium chloride, and agreeing with it in all other respects—in colour, crystalline habit, behaviour towards solvents and towards sodium hydroxide. Finally, the melting point of the mixture ($210-212^{\circ}$) definitely established the identity of the two products.

Synthesis of 5-amino-2-pyridone.

Ethyl hydroxynicotinate, $\text{CO}_2\text{Et}\cdot\text{C}_5\text{H}_4\text{N}\cdot\text{OH}$, is readily prepared by heating a solution of the acid in twenty parts of absolute alcohol for six hours in a stream of hydrogen chloride under a reflux condenser. The alcohol is evaporated under reduced pressure, and the residue neutralised with sodium hydrogen carbonate, when the ester is obtained as a white, crystalline substance which, when crystallised several times from hot water, separates in lustrous white needles melting at $149-150^{\circ}$. The yield is about 75 per cent. of the theoretical:

0.1754 gave 12.8 c.c. N_2 at 18° and 752 mm. $\text{N} = 8.34$.

$\text{C}_8\text{H}_9\text{O}_3\text{N}$ requires $\text{N} = 8.38$ per cent.

Hydroxynicotinic hydrazide, $\text{NH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{C}_5\text{H}_4\text{N}\cdot\text{OH}$.—Ethyl hydroxynicotinate is mixed with enough 50 per cent. solution of hydrazine hydrate to moisten it thoroughly, and heated on a water-bath; after a few minutes a clear solution is formed from which, on continued heating, the *hydrazide* separates as a white solid. After about twenty minutes' heating the mixture is cooled, the product collected, washed with a little cold alcohol, and then crystallised a few times from boiling alcohol, in which it is rather sparingly soluble. It is readily soluble in water or glacial acetic acid, but sparingly so in the other common organic solvents. Its aqueous solution gives a yellow coloration with ferric chloride, and reduces Fehling's solution on heating. The substance has no definite melting point. It remains

white up to 288° , begins to darken above this point, and is completely melted at 310° :

0.1934 gave 43.4 c.c. N_2 at 7° and 766 mm. $N = 27.44$.

$C_6H_7O_4N_2$ requires $N = 27.45$ per cent.

Hydroxynicotinic azide, $N_3 \cdot CO \cdot C_5NH_3 \cdot OH$.—The hydrazide is dissolved together with a molecular proportion of sodium nitrite in a 12 per cent. solution of sodium hydroxide, and the mixture added drop by drop to the equivalent quantity of ice-cold dilute hydrochloric acid. The azide separates during the operation as a white solid. It is collected, dried, and crystallised from benzene.

When freshly prepared it is white, but turns pink in the vacuum desiccator, and gave a somewhat low result on analysis.

It melts and decomposes at 139 – 140° :

0.0826 gave 23.0 c.c. N_2 at 12.3° and 768 mm. $N = 33.36$.

$C_6H_4O_2N_4$ requires $N = 34.15$ per cent.

Bishydroxypyridylcarbamide, $CO(NH \cdot C_5NH_3 \cdot OH)_2$.—On boiling hydroxynicotinic azide with water, nitrogen is evolved, and the solution gradually becomes deep red. The gas evolution ceases after about three-quarters of an hour. The liquid is then cooled and the carbamide crystallises out. Even after repeated crystallisation from water, the substance retains traces of pink colouring matter. It begins to darken at about 270° , and finally decomposes at about 302° :

0.0627 gave 12.0 c.c. N_2 at 16° and 758 mm. $N = 22.3$.

$C_{11}H_4O_3N_4$ requires $N = 22.8$ per cent.

The substance is readily soluble in methyl and ethyl alcohols or hot water, but sparingly so in the other common solvents.

On boiling the azide with absolute alcohol for half an hour, a crystalline substance was obtained which, after four crystallisations from acetone, melted at 219 – 222° . This was doubtless the urethane $CO_2Et \cdot NH \cdot C_5NH_3 \cdot OH$, but since it appeared even less easy to purify than the carbamide it was not further investigated.

5-amino-2-pyridone, $NH_2 \cdot C_5H_4ON$.—The crude hydrochloride of this base may be obtained either by hydrolysis of the carbamide just described or from 2-chloro-5-aminopyridine. The carbamide is heated in a sealed tube with concentrated hydrochloric acid to 125° for eight hours. After opening the tube (in which the presence of carbon dioxide can be readily demonstrated) the solution is concentrated, and the crude hydrochloride is obtained as a reddish syrup which, on standing in a desiccator, sets to a crystalline mass.

The same substance is obtained from 2-chloro-5-aminopyridine by heating it to 120 – 125° for twenty-four hours with a methyl-alcoholic solution of sodium methoxide.

On opening the tube the alkali is quickly neutralised by the addition

of a slight excess of a methyl-alcoholic solution of hydrogen chloride. The aminopyridone oxidises with extreme rapidity in alkaline solution with the production of a deep purple colour. After filtering from the precipitated sodium chloride and evaporating the alcohol, the crude hydrochloride of the aminopyridone is obtained in a form similar to that produced by the former method.

Since no means of satisfactorily purifying this hydrochloride was found, and since the solubility of the free base in water, together with its proneness to oxidation, made it clear that it would not be possible to isolate it in a pure state without considerable expenditure of material, some other means of characterising it was sought for, and was found in its ready conversion into a crystalline benzoyl derivative.

If the crude hydrochloride, obtained by either method, is dissolved in sodium hydrogen carbonate solution and shaken for half an hour with excess of benzoyl chloride, a white substance is obtained which, after washing with ether, crystallises from alcohol in pure white needles melting at 212.5° . The yield is, however, somewhat disappointing.

The analysis of the substance taken together with its two modes of formation proves it to be of 5-benzoylamino-2-pyridyl benzoate:

0.1451 gave 0.3851 CO_2 and 0.0578 H_2O . $\text{C} = 72.0$; $\text{H} = 4.4$.

0.1398 „ 10.4 c.c. N_2 at 15.5° and 777 mm. $\text{N} = 8.9$.

$\text{C}_{19}\text{H}_{14}\text{O}_3\text{N}_2$ requires $\text{C} = 71.7$; $\text{H} = 4.4$; $\text{N} = 8.8$ per cent.

The same compound is readily formed by benzoylation of the aminopyridone in pyridine solution. The crude hydrochloride of aminopyridone, prepared from 2-chloro-5-aminopyridine, was dissolved in pyridine and an excess of benzoyl chloride added. A heavy white precipitate of pyridine hydrochloride was rapidly formed. After a quarter of an hour, the mixture was treated with sufficient water to dissolve the pyridine, when an oil separated consisting of the excess of benzoyl chloride containing the benzoyl compound in solution. On separating the oil and adding ether (in which it is very slightly soluble), the benzoyl compound crystallised in needles which after single crystallisation from alcohol melted at $211-212^{\circ}$.

5-Benzoylamino-2-pyridyl benzoate is practically insoluble in water and almost so in ether. It dissolves readily in chloroform and can be recrystallised from benzene, but with greater advantage from alcohol. The following facts seem to show that the O-benzoyl group is readily eliminated by alcoholic potash. The substance was mixed with an alcoholic solution of potassium hydroxide and left for twenty-four hours at the ordinary temperature. After addition of water, the alcohol was distilled off and the alkaline liquid saturated with carbon

dioxide, whereupon a substance was precipitated which was sparingly soluble in ether or benzene, and readily so in alcohol or hot water. After recrystallisation from the latter solvent it melted at 252–253°. The quantity of the substance thus obtained was unfortunately insufficient for analysis, but since it thus possesses phenolic properties, and on acidification of the residual liquid with hydrochloric acid a substance crystallised, which from its melting point (120°) and other characteristics was readily identified as benzoic acid, it was in all probability 5-benzoylamino-2-pyridone, $C_6H_5 \cdot CO \cdot NH \cdot C_5H_4ON$. It was also once obtained accidentally by the incomplete benzoylation of the aminopyridone.

Reduction of 5-Benzeneazo-2-pyridone.

Benzeneazopyridone is dissolved in boiling alcohol, and a concentrated aqueous solution of sodium hyposulphite gradually added. The colour of the liquid rapidly diminishes up to a certain point, at which addition of more hyposulphite produces no further visible change. The alcohol and aniline produced in the reaction are then removed by a current of steam or by extraction with ether after rendering alkaline with sodium hydroxide, and the residual liquid shaken for half an hour with benzoyl chloride after the addition of either sodium hydroxide or sodium hydrogen carbonate. There is then precipitated the same substance as is produced by treating aminopyridone with benzoyl chloride. After purification by washing with ether and recrystallising from alcohol, this was unmistakably identified by its general characteristics, its melting point (210–211°) and "mixed" melting point (210·5–211·5°), as 5-benzoylamino-2-pyridyl benzoate.

In conclusion, we have to express our indebtedness to the Government Grant Committee of the Royal Society for a grant by which the expenses of this investigation have been largely defrayed.

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CXXXII.—*Aromatic Selenonium Bases.*

By THOMAS PERCY HILDITCH and SAMUEL SMILES.

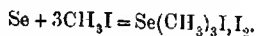
THE preparation of aromatic sulphonium bases has been described by Smiles and Le Rossignol (*Trans.*, 1906, **89**, 696; *Proc.*, 1906, 22, 158; *Trans.*, 1908, **93**, 745), and it has been shown that three

general methods exist by means of which such compounds may be obtained:

- (1) The action of thionyl chloride on a phenolic ether (or other suitable aromatic compound) in presence of aluminium chloride;
- (2) the action of sulphur dioxide on such compounds in presence of aluminium chloride;
- (3) the condensation of an aromatic sulphinic acid or sulphoxide with a phenolic ether in presence of an appropriate dehydrating agent, usually concentrated sulphuric acid.

The last procedure has also been applied by the present authors to the preparation of mixed fatty aromatic sulphonium derivatives in the case of camphor- β -sulphinic acid (*Trans.*, 1907, 91, 519), and it appeared likely that members of the hitherto unknown class of aromatic selenonium bases could be obtained by a modification of one of these methods.

Purely aliphatic selenonium derivatives have been known for many years; Jackson (*Annalen*, 1875, 179, 1) prepared trimethylselenonium iodide and benzyldimethylselenonium iodide by the interaction of dibenzyl diselenide and methyl iodide, whilst the corresponding triethylselenonium iodide was obtained by Pieverling (*Annalen*, 1877, 185, 331) from ethyl selenomercaptan and ethyl iodide; by means of moist silver oxide this substance was transformed into a base possessing a strongly alkaline reaction. Scott (*Proc.*, 1904, 20, 156) showed that by heating selenium or tellurium with methyl iodide in sealed tubes at 180° periodides of the aliphatic bases were formed, thus:



The only aromatic compounds containing quadrivalent selenium noticed up to the present appear to be phenyl selenoxide and phenylselenonic acid. Diphenyl diselenide, $(\text{C}_6\text{H}_5)_2\text{Se}_2$, yields diphenylselenium dibromide, $(\text{C}_6\text{H}_5)_2\text{SeBr}_2$, when acted on by bromine, and this substance, treated with aqueous sodium hydroxide, gives diphenyl selenoxide, $(\text{C}_6\text{H}_5)_2\text{SeO}$ (Krafft and Vorster, *Ber.*, 1893, 26, 2813); whereas, if the original diselenide is oxidised with nitric acid phenylseleninic acid, $\text{C}_6\text{H}_5\cdot\text{SeO}_2\text{H}$, results (Stoecker and Krafft, *Ber.*, 1906, 39, 2197), whilst phenylselenonic acid, $\text{C}_6\text{H}_5\cdot\text{SeO}_3\text{H}$, is formed when chlorine is used as the oxidising agent.

The production of aromatic compounds containing basic selenium—a preliminary account of which has been communicated to the Society (*Proc.*, 1907, 23, 12)—has been effected by the action of selenium dioxide on certain phenolic ethers in presence of aluminium chloride. It is probable, judging from the corresponding sulphur analogues of these compounds (Smiles and Le Rossignol, *loc. cit.*), that by using phenolic ethers suitably substituted in the benzene nucleus, new

aromatic selenoxides and seleninic acids would be obtained, but we have confined our attention solely to those ethers likely to yield the selenium derivatives. It is noteworthy that selenium dioxide reacts much less readily than sulphur dioxide, for whilst the action of the latter had to be regulated by use of a freezing mixture, in the case of selenium dioxide it was necessary to heat the mixture on the water-bath.

The aromatic selenonium bases as a class are stable, strongly basic substances, their salts resembling the corresponding sulphonium derivatives in their stability towards aqueous sodium hydroxide. These, however, are for the most part non-crystalline or can only be obtained crystalline with the greatest difficulty; the chlorides are fairly soluble in water, the iodides sparingly so. In consequence of the amorphous nature of most of the compounds belonging to this group, we have only been able to obtain a few of them sufficiently pure for analysis; but the results obtained leave no doubt as to their constitution.

EXPERIMENTAL.

Triphenetylselenium ($C_6H_4 \cdot O \cdot C_2H_5$)₃Se.

Eight grams of powdered aluminium chloride were dissolved in 10 grams of phenetole, the mixture being kept cool; 3 grams of powdered selenium dioxide were then added, but no reaction took place until heat was applied. On warming on the water-bath, however, hydrogen chloride was evolved copiously and the reaction mixture soon became pasty and finally almost solid. After one hour the product was decomposed with ice and any excess of phenetole was removed by distillation with steam. The residue was next extracted with chloroform, and this extract dried and evaporated; the substance left was redissolved in alcohol and boiled with animal charcoal, when, after filtering and evaporating in a vacuum at the ordinary temperature, *triphenetylselenium chloride* ($C_6H_4 \cdot O \cdot C_2H_5$)₃SeCl, was left as an almost colourless semi-solid mass, the yield being fairly good.

Triphenetylselenium Hydroxide.—Boiling aqueous sodium hydroxide had little or no effect on the chloride, but on boiling about 60 grams of this substance in alcoholic solution with dry freshly-precipitated silver oxide for a few minutes and removing the silver chloride and oxide, a solution of the base was obtained. This showed a strongly alkaline reaction towards litmus; the hydroxide was not precipitated from solution by water, and closely resembles the triphenetylsulphonium base. On exactly neutralising the base with hydriodic acid and evaporating the solution in a vacuum, the iodide was obtained as a pale yellow oil which could not be solidified.

Triphenetylselenium platinichloride was obtained in brown flakes

by adding a slight excess of platinum tetrachloride to the chloride dissolved in alcohol and then precipitating the product with excess of water. The substance was purified for analysis by twice redissolving in the least possible amount of acetone and then pouring the filtered solution into excess of water. It is exceedingly soluble in acetone and alcohol, and melts and decomposes at about 82—83°:

0.2022 gave 0.0304 Pt. Pt = 15.03.

0.1790 „ 0.2897 CO₂ and 0.0701 H₂O. C = 44.14; H = 4.35.

(C₂₄H₂₇O₃Se)₂PtCl₆ requires Pt = 15.09; C = 44.58; H = 4.18 per cent

Trianisylselenium (C₆H₄·O·CH₃)₃Se.

Trianisylselenium chloride was prepared from anisole, selenium dioxide, and aluminium chloride by an analogous method to that used for the phenetyl compound, and remained as a dark uncrystallisable oil on evaporation of its solutions in a vacuum. The *hydroxide* and *iodide* are quite similar to those of triphenylselenium; the *platinichloride* is a brown amorphous body decomposing below 90° and not very stable at the ordinary temperature.

The *dichromate* was also prepared by mixing the alcoholic solution of the chloride with acidified potassium dichromate solution; a brown precipitate formed, which was at once collected and purified by solution in acetone and reprecipitation by excess of water. It is an orange-brown powder decomposing at 68—70°:

0.2206 gave 0.0320 Cr₂O₃. Cr = 9.93.

(C₂₁H₂₁O₃Se)₂Cr₂O₇ requires Cr = 10.24 per cent.

Hexamethyltrirosocylselenium [C₆H₃(O·CH₃)₂]₃Se.

The condensation of resorcinol dimethyl ether with selenium dioxide was also attempted, and the chloride was obtained as a pinkish semi-solid mass, but a considerable quantity of other substances was also formed, and as the separation and purification of the selenium compounds was exceedingly difficult, the investigation of the base from this ether was not pursued further.

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CXXXIII.—*The Relation Between Unsaturation and Optical Activity. Part III. Optically Active Salts of Acids Containing Adjacent Unsaturated Groups.*

By THOMAS PERCY HILDITCH.

• IT is a fairly well-established rule that the presence of an ethylenic or of an acetylenic linking in an optically active compound tends to increase the rotatory power beyond that of the corresponding saturated compound; but this statement must always be coupled with the reservation, that, since optical activity is a physical property extremely susceptible to changes of constitution, apparent exceptions to the general rule may not unnaturally be met with in cases in which the structure of the substances under observation is somewhat complicated. Examples of such exceptions are to be noticed in the case of various esters of menthol and borneol examined by Hartwall (*Dis.*, Helsingfors, 1904) and by the author (*Trans.*, 1908, 93, 1). With unsaturated groups, then, other than those associated with a minimum change in the molecule of constitution and of mass, one would not necessarily expect to observe such definite effects as in the latter instance; at the same time, the presence of groups possessing a considerable degree of residual affinity frequently appears to be accompanied by increase in rotatory power.

For example, the rotatory power of menthol and of some of its esters are given in the following table:*

	$[\alpha]_D$	$[M]_D$
Menthol, $C_{10}H_{18}OH$	-48.92	-76.3
Menthyl acetate, $CH_3CO_2C_{10}H_{19}$	79.52	157.5
„ propionate, $C_3H_7CO_2C_{10}H_{19}$	75.51	160.1
„ butyrate, $C_4H_9CO_2C_{10}H_{19}$	69.52	157.1
„ β -phenylpropionate, $C_6H_5CH_2CH_2CO_2C_{10}H_{19}$	56.21	161.9
„ phenylacetate, $C_6H_5CH_2CO_2C_{10}H_{19}$	69.60	190.7
„ benzoate, $C_6H_5CO_2C_{10}H_{19}$	90.90	236.3
„ carbamate, $NH_2CO_2C_{10}H_{19}$	85.11	168.3
„ carbonate, $CO_2OC_{10}H_{19}$	92.52	312.7

. Again, it was shown in Part II of this series that the rotatory powers of esters and salts of cinnamic and phenylpropionic acids diverged more widely from those of the original bases than those of the other acids investigated; the following are the specific rotations of amyl esters of these acids as measured by Walden (*Zeitsch. physikal.*

* The references to the data from which the above values are obtained have already been given in a previous part of this series.

Chem., 1896, 20, 569) and of their salts with various alkaloids (Part II, *loc. cit.*):

Base.	β -Phenyl- propionate.	Cinna- mate.	Phenyl- propionate.	Succinate.	Fumarate.
Amyl	-4.8	+2.3	+7.5	+5.5	+3.76
Brucine	-122.0	-38.2	-11.7	+3.3	-68.8
Cinchonine	+222.0	+116.3	+107.5	+86.0	+159.0
Cocaine	-116.0	-64.4	-51.6	-51.0	-87.8
Couline	+8.0	-1.9	-7.5	-7.1	+5.1
					+4.0

It is significant that in the above salts an exceptional alteration in optical activity always coincides with the presence in the molecule of two conjugated unsaturated groups next to the carboxyl group, and that, with the esters to which attention has just been drawn, it is only those containing two such groups in close proximity to each other and to the optically active part of the molecule which show abnormal values for the rotatory power. Thus menthyl acetate, propionate, butyrate, β -phenylpropionate, and carbonate possess molecular rotations varying between comparatively small limits, -157° to -162° . If, however, another unsaturated residue is placed adjacent to the carboxyl group, exaltation of the rotatory power takes place. This is well marked in the case of menthyl benzoate, where a phenyl and a carboxyl group are situated side by side; neither of these groups behaves abnormally when separated by a chain of saturated radicles, for the corresponding ester of β -phenylpropionic acid has almost the average rotation of an ordinary menthyl ester, but as the phenyl group is moved up to the carboxyl, the effect of these two groups acting in conjunction becomes apparent, the values for menthyl phenylacetate and benzoate showing progressive increases on the normal molecular rotation of menthyl esters.

Again, menthyl carbamate exhibits a slight exaltation, due presumably to the conjugation of the amino- and carboxyl-groups; and Cohen and Armes (*Trans.*, 1905, 87, 1190) have observed that the molecular rotations of the isomeric nitrobenzoic menthyl esters are much greater than those of the corresponding chloro- or iodo-benzoic esters or of menthyl benzoate. This effect may similarly be ascribed to the presence of the nitro-group, rich in residual affinity, and directly united to the phenyl group.

The present investigation includes the preparation and polarimetric measurement of a series of alkaloid salts of acids containing one, two, three, and four contiguous unsaturated groups in the molecule, and also of benzoic, phenylacetic, and β -phenylpropionic acids; the latter series is of interest in affording further evidence that as the distance between two unsaturated groups increases, the optical anomaly diminishes. The alkaloids used were brucine and cinchonine, and the rotatory powers of the free bases have been given in Part II of this

series, the same specimens being used in both investigations. The acids used were purified by recrystallisation until they possessed the correct melting point before being used to prepare the various salts.

The results obtained serve on the whole to justify the conclusion that contiguous unsaturated groups exert an abnormal influence on the optical rotatory power of a compound. The salts of brucine show a more consistent series of variations than those of cinchonine, for the presence of an unsaturated group adjacent to the acidic part of the molecule appears to have a quite unusual result in the case of this alkaloid; since the latter base is di-acidic, both possible series of its salts have in some cases been prepared, and the same order is observed to hold with both mono- and di-acid salts for each series of increasingly unsaturated acids. It is noteworthy, too, that the rotatory powers of solutions in chloroform of those cinchonine salts possessing the abnormal values just mentioned increase rapidly as the concentration of the solution diminishes.

EXPERIMENTAL.

The salts used were prepared by mixing equivalent quantities of base and acid in boiling water or alcohol, filtering and setting aside to cool or evaporate as circumstances required. After a single recrystallisation the substances were sufficiently pure for polarimetric measurement.

Brucine Benzotate, $C_{22}H_{26}O_4N_2 \cdot C_7H_5O_2 \cdot 2\frac{1}{2}H_2O$.

Small white crystals, readily soluble in water and alcohol, melting at 94.5° :

0.1894 gave 0.4444 CO_2 and 0.1206 H_2O . $C = 63.98$; $H = 7.07$.

$C_{30}H_{33}O_6N_2 \cdot 2\frac{1}{2}H_2O$ requires $C = 64.16$; $H = 6.60$ per cent.

Brucine Phenylacetate, $C_{23}H_{26}O_4N_2 \cdot C_8H_7O_2 \cdot 1\frac{1}{2}H_2O$.

Square tablets, somewhat efflorescent, melting at $130-131^\circ$:

0.1160 gave 0.2848 CO_2 and 0.0698 H_2O . $C = 66.94$; $H = 6.69$.

$C_{31}H_{34}O_6N_2 \cdot 1\frac{1}{2}H_2O$ requires $C = 66.77$; $H = 6.64$ per cent.

Brucine Anthranilate, $C_{23}H_{26}O_4N_2 \cdot C_7H_7O_2N \cdot 1\frac{1}{2}H_2O$.

Small cream-coloured crystals, soluble in water and alcohol, melting at 132° :

0.1868 gave 0.4438 CO_2 and 0.1074 H_2O . $C = 64.79$; $H = 6.39$.

$C_{30}H_{33}O_6N_3 \cdot 1\frac{1}{2}H_2O$ requires $C = 64.52$; $H = 6.45$ per cent.

This salt separates from alcohol with 1 molecule of alcohol of crystallisation. A sample prepared from alcohol was analysed:

0.1784 gave 0.4362 CO_2 and 0.1132 H_2O . $\text{C} = 66.68$; $\text{H} = 7.05$.
 $\text{C}_{30}\text{H}_{28}\text{O}_6\text{N}_2 \cdot \text{C}_7\text{H}_5\text{O}$ requires $\text{C} = 66.55$; $\text{H} = 6.76$ per cent.

Brucine Acetylanthranilate, $\text{C}_{23}\text{H}_{26}\text{O}_4\text{N}_2 \cdot \text{C}_9\text{H}_9\text{O}_3\text{N}$, $1\frac{1}{2}\text{H}_2\text{O}$.

White nodules, fairly soluble in water, melting and foaming at $95-97^\circ$:

0.1179 gave 0.2756 CO_2 and 0.0720 H_2O . $\text{C} = 63.75$; $\text{H} = 6.79$.
 $\text{C}_{32}\text{H}_{38}\text{O}_7\text{N}_3$, $1\frac{1}{2}\text{H}_2\text{O}$ requires $\text{C} = 64.00$; $\text{H} = 6.33$ per cent.

Brucine Benzoylanthranilate, $\text{C}_{23}\text{H}_{26}\text{O}_4\text{N}_2 \cdot \text{C}_{14}\text{H}_{11}\text{O}_3\text{N}$, $4\frac{1}{2}\text{H}_2\text{O}$.

Clusters of white needles, melting and foaming at 108° :

0.1650 gave 0.3752 CO_2 and 0.0926 H_2O . $\text{C} = 62.00$; $\text{H} = 6.24$.
 $\text{C}_{37}\text{H}_{37}\text{O}_7\text{N}_3$, $4\frac{1}{2}\text{H}_2\text{O}$ requires $\text{C} = 62.01$; $\text{H} = 6.42$ per cent.

Brucine Salicylate, $\text{C}_{23}\text{H}_{26}\text{O}_4\text{N}_2 \cdot \text{C}_7\text{H}_6\text{O}_3$.

Fine white needles, sparingly soluble in water and alcohol, melting and decomposing at $250-254^\circ$:

0.1700 gave 0.4212 CO_2 and 0.0864 H_2O . $\text{C} = 67.57$; $\text{H} = 5.65$.
 $\text{C}_{30}\text{H}_{32}\text{O}_7\text{N}_2$ requires $\text{C} = 67.67$; $\text{H} = 6.01$ per cent.

Brucine Acetylsalicylate, $\text{C}_{23}\text{H}_{26}\text{O}_4\text{N}_2 \cdot \text{C}_9\text{H}_8\text{O}_4$.

Transparent rectangular prisms, fairly soluble in water and alcohol, melting and decomposing at 251° :

0.1470 gave 0.3617 CO_2 and 0.0802 H_2O . $\text{C} = 67.10$; $\text{H} = 6.06$.
 $\text{C}_{32}\text{H}_{34}\text{O}_8\text{N}_2$ requires $\text{C} = 66.89$; $\text{H} = 5.93$ per cent.

Brucine Benzoylsalicylate, $\text{C}_{23}\text{H}_{26}\text{O}_4\text{N}_2 \cdot \text{C}_{14}\text{H}_{10}\text{O}_4$, H_2O .

Hard white prisms, moderately insoluble in water, sparingly so in alcohol, fusing at $103-106^\circ$, resolidifying and melting finally at 148° :

0.1588 gave 0.3974 CO_2 and 0.0840 H_2O . $\text{C} = 68.23$; $\text{H} = 5.88$.
 $\text{C}_{37}\text{H}_{36}\text{O}_8\text{N}_2$, H_2O requires $\text{C} = 67.90$; $\text{H} = 5.81$ per cent.

Cinchonine Benzoate, $\text{C}_{19}\text{H}_{22}\text{ON}_2 \cdot \text{C}_7\text{H}_6\text{O}_3$.

Thin prisms, from alcohol, melting at 186° :

0.1218 gave 0.3338 CO_2 and 0.0785 H_2O . $\text{C} = 74.73$; $\text{H} = 7.16$.
 $\text{C}_{26}\text{H}_{28}\text{O}_3\text{N}_2$ requires $\text{C} = 75.00$; $\text{H} = 6.73$ per cent.

Cinchonine Dibenzoate, $C_{19}H_{22}ON_2 \cdot 2C_6H_5O_2 \cdot 2H_2O$.

Small prisms, very deliquescent in air, melting at 145° :

0.1897 gave 0.4787 CO_2 and 0.1126 H_2O . $C = 68.81$; $H = 6.60$.

$C_{33}H_{34}O_5N_2 \cdot 2H_2O$ requires $C = 68.98$; $H = 6.62$ per cent.

Cinchonine Diphenylacetate, $C_{19}H_{22}ON_2 \cdot 2C_6H_5O_2 \cdot 2\frac{1}{2}H_2O$.

An oil which solidified slowly to a horny mass, but did not crystallise:

0.1596 gave 0.4018 CO_2 and 0.1060 H_2O . $C = 68.64$; $H = 7.38$.

$C_{35}H_{38}O_5N_2 \cdot 2\frac{1}{2}H_2O$ requires $C = 68.74$; $H = 7.04$ per cent.

Cinchonine Anthranilate, $C_{19}H_{22}ON_2 \cdot C_7H_7O_2N$.

Small cream-coloured prisms from alcohol, melting at $165-167^\circ$:

0.2078 gave 0.5495 CO_2 and 0.1307 H_2O . $C = 72.11$; $H = 6.98$.

$C_{26}H_{26}O_3N_3$ requires $C = 72.40$; $H = 6.73$ per cent.

Cinchonine Dianthranilate, $C_{19}H_{22}ON_2 \cdot 2C_7H_7O_2N \cdot 2\frac{1}{2}H_2O$.

A cream-coloured microcrystalline powder, melting and losing water at $97-98^\circ$:

0.1376 gave 0.3255 CO_2 and 0.0861 H_2O . $C = 64.52$; $H = 6.95$.

$C_{33}H_{36}O_5N_4 \cdot 2\frac{1}{2}H_2O$ requires $C = 64.60$; $H = 6.69$ per cent.

Cinchonine Acetylanthranilate, $C_{19}H_{22}ON_2 \cdot C_9H_9O_3N$.

Square tablets precipitated from alcohol by ether, melting at $195-196^\circ$:

0.1337 gave 0.3497 CO_2 and 0.0806 H_2O . $C = 71.32$; $H = 6.70$.

$C_{28}H_{31}O_4N_3$ requires $C = 71.04$; $H = 6.55$ per cent.

Cinchonine Diacetylanthranilate, $C_{19}H_{22}ON_2 \cdot 2C_9H_9O_3N \cdot 1\frac{1}{2}H_2O$.

A deliquescent crystalline mass, melting and foaming at 100° :

0.1940 gave 0.4640 CO_2 and 0.1090 H_2O . $C = 65.22$; $H = 6.25$.

$C_{37}H_{40}O_7N_4 \cdot 1\frac{1}{2}H_2O$ requires $C = 65.39$; $H = 6.33$ per cent.

Cinchonine Benzoylanthranilate, $C_{19}H_{22}ON_2 \cdot C_{14}H_{11}O_3N \cdot \frac{1}{2}H_2O$.

Small needles, soluble in water and in alcohol, melting at 144° :

0.1469 gave 0.3902 CO_2 and 0.0832 H_2O . $C = 72.44$; $H = 6.29$.

$C_{33}H_{35}O_4N_3 \cdot \frac{1}{2}H_2O$ requires $C = 72.80$; $H = 6.25$ per cent.

Cinchonine Dibenzoanthranilate, $C_{19}H_{22}ON_2 \cdot 2C_{14}H_{11}O_2N \cdot 6H_2O$.

Slightly deliquescent prisms, melting and decomposing at $104-105^\circ$:

0.1962 gave 0.4592 CO_2 and 0.1140 H_2O . $C = 63.86$; $H = 6.46$.

$C_{47}H_{44}O_7N_4 \cdot 6H_2O$ requires $C = 63.80$; $H = 6.33$ per cent.

Cinchonine Salicylate, $C_{19}H_{22}ON_2 \cdot C_7H_6O_3$.

Large white prisms, soluble in water and alcohol, melting at 164° :

0.1392 gave 0.3687 CO_2 and 0.0801 H_2O . $C = 72.23$; $H = 6.39$.

$C_{26}H_{28}O_4N_2$ requires $C = 72.22$; $H = 6.48$ per cent.

Cinchonine Acetylsalicylate, $C_{19}H_{22}ON_2 \cdot C_9H_8O_4 \cdot \frac{1}{2}H_2O$.

An oil which solidified in a vacuum to a mass of small needles, melting at 80° :

0.1527 gave 0.3897 CO_2 and 0.0936 H_2O . $C = 69.60$; $H = 6.81$.

$C_{18}H_{20}O_5N_2 \cdot \frac{1}{2}H_2O$ requires $C = 69.56$; $H = 6.42$ per cent.

Cinchonine Benzoylsalicylate, $C_{19}H_{22}ON_2 \cdot C_{14}H_{10}O_4 \cdot \frac{1}{2}H_2O$.

An oil, which solidified in a vacuum to thin white leaflets, melting at 158° :

0.1612 gave 0.4303 CO_2 and 0.0906 H_2O . $C = 72.81$; $H = 6.24$.

$C_{33}H_{32}O_5N_2 \cdot \frac{1}{2}H_2O$ requires $C = 72.66$; $H = 6.06$ per cent.

The polarimetric observations were made in dry chloroform solution in a 2-dm. tube, the temperature, except where otherwise indicated, being 21° . The following tables show the specific and molecular rotatory powers obtained for each salt, together with those of the free bases. The first table deals with those acids containing two unsaturated groups at varying distances from each other in the molecule; the effect observed in the case of brucine salts diminishes progressively as the phenyl group is moved away from the carboxyl residue, whilst with cinchonine benzoate, as previously mentioned, an altogether abnormal value obtains.

TABLE I.

Acid. Percentage concentration:	Brucine salt.				Cinchonine di-acid salt.			
	5.		2½.		5.		2½.	
	$[\alpha]_D$.	$[M]_D$.	$[\alpha]_D$.	$[M]_D$.	$[\alpha]_D$.	$[M]_D$.	$[\alpha]_D$.	$[M]_D$.
Benzoic	-122.0	-480.7	-122.0	-480.7	+222.0	+652.7	+222.0	+652.7
Phenyl-	-25.4	-131.1	-25.0	-129.0	+151.0	+812.5	+163.0	+877.0
acetic	-30.5	-161.7	-32.2	-170.7	+107.0	+605.6	+109.0	+616.9
6 Phenyl-	-38.2	-207.7	-38.5	-209.2	+116.2	+690.7	+120.5	+715.7
napionic								

* Temperature = 20° .

Two series of acids containing contiguous unsaturated groups have been used, one consisting of anthranilic, acetyl-anthranilic, and benzoyl-anthranilic acids, the other of the corresponding derivatives of salicylic acid. It is obvious that in each case there are acids containing successively two, three, and four groups possessing varying degrees of residual affinity united to the carboxyl residue in the molecule; at the same time it must be remembered that the molecular weight of members of the series varies somewhat widely, and therefore the rotations observed can only be interpreted as a somewhat rough indication of the effect of conjugated unsaturated groups. It is hoped that the results of measurements of derivatives of acids containing conjugated ethylenic linkings (which involve minimum change of molecular weight) will shortly be ready for publication. In the meantime, as the following tables show, it is clear that increase in the number of adjacent unsaturated groups tends to increase the optical effect.

TABLE II.

Acid. Percentage concentration :	Brucine salt.				Cinchonine mono-acid salt.			
	5.		2½.		5.		2½.	
	[α] _D .	[M] _D .	[α] _D .	[M] _D .	[α] _D .	[M] _D .	[α] _D .	[M] _D .
Benzolic ...	-122.0	-480.7	-122.0	-480.7	+222.0	+652.7	+222.0	+652.7
Anthranilic ...	-25.4	-131.1	-25.0	-129.0	+141.1	+587.0	+163.0	+678.1
Acetyl-anthranilic ...	-9.0	-47.8	-8.8	-46.7	+162.8	+701.7	+176.8	+761.1
Benzoyl-anthranilic ...	+5.2	+29.8	+5.0	+28.7	+125.8	+595.0	+141.2	+667.9
Benzoyl-anthranilic ...	+24.6	+156.2	+24.4	+154.9	+144.2	+771.5	+161.8	+865.6

Acid.	Cinchonine di-acid salt.			
	5.		2½.	
	[α] _D .	[M] _D .	[α] _D .	[M] _D .
Benzolic	+222.0	+652.7	+222.0	+652.7
Anthranilic	+151.0	+812.5	+163.0	+877.0
Acetyl-anthranilic	+161.4	+916.6	+173.0	+982.4
Benzoyl-anthranilic	+111.3	+725.4	+121.6	+792.7
Benzoyl-anthranilic	+113.8	+883.1	+122.6	+951.5

TABLE III.

Acid. Percentage concentration :	Brucine salt.				Cinchonine mono-acid salt.			
	5.		2½.		5.		2½.	
	[α] _D .	[M] _D .	[α] _D .	[M] _D .	[α] _D .	[M] _D .	[α] _D .	[M] _D .
Benzolic ...	-122.0	-480.7	-122.0	-480.7	+222.0	+652.7	+222.0	+652.7
Salicylic ...	-25.4	-131.1	-25.0	-129.0	+141.1	+587.0	+163.0	+678.1
Acetyl-salicylic ...	+14.2	+75.5	+11.6	+77.7	+142.3	+614.7	+157.8	+681.7
Benzoyl-salicylic ...	+15.1	+86.7	+15.6	+89.5	+135.0	+640.0	+142.8	+676.9
Benzoyl-salicylic ...	±0.1	±0.6	±0.0	±0.0	+137.3	+735.9	+156.0	+826.2

The author wishes to express his gratitude to Professor Collie and Assistant-Professor Smiles for the interest they have shown in this work.

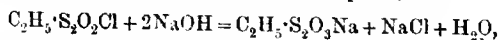
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CXXXIV.—*The Preparation of Disulphides. Part II.* *The Action of Alkalis on Sodium Alkyl Thiosulphates.*

By THOMAS SLATER PRICE and DOUGLAS FRANK TWISS.

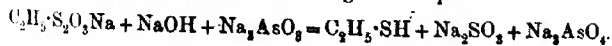
IN a previous paper (Trans., 1907, 91, 2021), a method has been described for the preparation of dibenzyl and diethyl disulphides by the electrolysis of the corresponding sodium alkyl thiosulphates in neutral or alkaline solution. Whilst endeavouring to extend this method to the preparation of the nitrobenzyl disulphides, it was found that the addition of alkali, preferably sodium carbonate, to the solution of a sodium nitrobenzyl thiosulphate causes a more or less rapid precipitation of the corresponding nitrobenzyl disulphide. The three nitrobenzyl disulphides have been isolated in this way, and the method of their preparation is described in the succeeding paper. These observations naturally led to an investigation of the action between alkalis and sodium ethyl and benzyl thiosulphates, with the result that the corresponding disulphide was obtained in each case.

At the time the above experiments were made, there was, as far as we could find, no experimental evidence concerning the action of alkalis on these organic thiosulphate compounds, which is surprising when one considers the time that has elapsed since their first isolation (Bunte, *Ber.*, 1874, 7, 646; Purgotti, *Gazzetta*, 1890, 20, 25). Spring (*Ber.*, 1874, 7, 1162) states that sodium hydroxide hydrolyses ethylthiosulphuryl chloride to sodium ethyl thiosulphate,



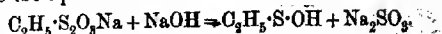
but mentions no further action:

Gutmann (*Ber.*, 1907, 40, 2818) refers to the subject in a paper on the action of sodium arsenite on sodium ethyl thiosulphate. The reaction takes place in alkaline solution with the formation of ethyl mercaptan and sodium arsenate according to the equation



In explanation of this reaction, Gutmann assumes the formation of

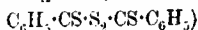
an intermediate compound, $C_6H_5 \cdot S \cdot OH$ (thioethyl hydroperoxide), according to the equation.



This intermediate compound then oxidises the arsenite to arsenate, being itself reduced to mercaptan at the same time. No experimental evidence is given for the existence of such an intermediate compound.*

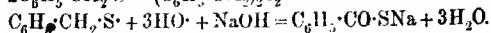
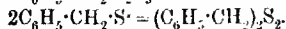
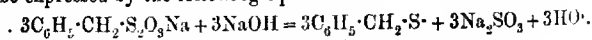
Our investigation of the action of alkalis on sodium ethyl and benzyl thiosulphates was practically complete when a paper was published by Gutmann on the same subject (*Ber.*, 1908, **41**, 1650). Since his results were not in agreement with ours, it has been necessary for us to test some of his conclusions.

Most of our experiments have been carried out with aqueous solutions of sodium benzyl thiosulphate. At the ordinary temperature the addition of sodium hydroxide, sodium carbonate, or ammonia causes the slow deposition of a white solid, which is dibenzyl disulphide. If the mixture is heated, the deposition is complete in less than an hour, but the separated disulphide, although fairly pure (m. p., without recrystallisation, 69° instead of 71°), is contaminated with a small quantity of a red substance (possibly thiobenzoyl disulphide,



which renders it pink. The yield of disulphide is always about 65 per cent., never more. The pale brown filtrate has a slight odour of mercaptan, which is probably due to the action of the sodium hydroxide on a very small proportion of the $C_6H_5 \cdot CH_2 \cdot S \cdot$ residues (see later) before these couple to form disulphide, aqueous sodium hydroxide being without action on free dibenzyl disulphide. The rest of the benzyl radicle forms sodium benzoate and thiobenzoate, which remain in solution. The inorganic products in the solution are sulphite, sulphide, and a small amount of sulphate. It is found that three molecules of sodium benzyl thiosulphate react with approximately four molecules of sodium and potassium hydroxides, giving approximately one molecule of dibenzyl disulphide.

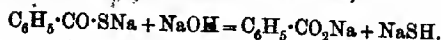
The reaction is probably very complicated, but the chief stages may be expressed by the following equations:



The third equation accounts for the fourth molecule of sodium hydroxide, but there are undoubtedly a number of subsidiary reactions

* At the end of the above paper, Gutmann mentions that he has found that iodine has no action on sodium ethyl thiosulphate. He has apparently overlooked the previous work on the subject (compare Slator, *Trans.*, 1904, **85**, 1286, *etc.*).

which occur at the same time. For example, some sodium hydrogen sulphide is formed from the sodium thiobenzoate,

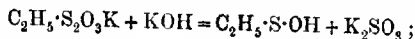


Also some sulphite is oxidised to sulphate by the hydroxyl groups represented in the above equations.

The fact that the three nitrobenzyl disulphides have been prepared in a similar manner, and that the yields never exceed 60 per cent. (although frequently less), constitutes a further confirmation of the above equations for the reaction in aqueous solution.

Qualitative experiments on the action between aqueous solutions of sodium hydroxide and sodium ethyl thiosulphate were also carried out. An oil separated, which was found to be diethyl disulphide.

Gutmann, in his last paper, gives the results of a quantitative investigation of the action of potassium hydroxide on sodium (or potassium), ethyl, amyl, and benzyl thiosulphates. The reactions were, however, carried out in alcoholic solution. The amounts of alkali used and of sulphite formed were in very good agreement with the equation



in no case was sulphate formed. In only one experiment was aqueous potassium hydroxide used, and then it was found that more alkali disappeared than corresponds with the above equation, which fact is in agreement with our results. Gutmann offers no explanation of this.

The hypothetical substance $\text{C}_2\text{H}_5\cdot\text{S}\cdot\text{OH}$ remains in solution (the potassium sulphite being insoluble in alcohol), and its characteristic reactions (in solution) are stated to be as follows: (1) The solution has only a very faint mercaptan odour,* unless water is added. (2) When heated with sodium arsenite, mercaptan and arsenate are formed. (3) Potassium thiocyanate is formed on digesting with a solution of potassium cyanide and sulphide.

In a footnote on p. 1653 he writes: "A solution of $\text{C}_2\text{H}_5\cdot\text{S}\cdot\text{OH}$ can also be obtained in the following manner. To a cold aqueous solution of sodium ethyl thiosulphate is added an excess of 50 per cent. sodium hydroxide and the mixture heated for some time at 40° . Most of the sulphite separates, and an oil swims on the aqueous solution. This oil gives the reactions with arsenite, cyanide, and sulphide." This footnote gave the clue to an explanation of Gutmann's results, since we had already found, as stated above, that this oil is diethyl disulphide. On further investigation, we have also found that the odour of diethyl disulphide becomes much fainter when dissolved in alcoholic

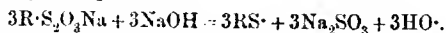
* Gutmann apparently confuses the odour of diethyl disulphide with that of ethyl mercaptan.

potash, and that, furthermore, it gives the above-mentioned reactions with arsenite, and with a mixture of cyanide and sulphide.

It would thus appear that the substance $C_2H_5 \cdot S \cdot OH$ has not been proved to exist, since diethyl disulphide accounts for all the reactions given. In further confirmation of this, we have isolated the compound formed by the interaction of sodium ethyl thiosulphate and potassium hydroxide in alcoholic solution; this solution should, according to Gutmann, contain the compound $C_2H_5 \cdot S \cdot OH$. However, on the addition of water and extraction with ether, diethyl disulphide was isolated and identified by its boiling point and by the formation of the characteristic addition compound with silver nitrate. The yield was poor, since it was somewhat difficult to separate the alcohol and the disulphide.

It seems probable that the mechanism of the action of alkalis on sodium alkyl thiosulphates is not the same for each of the latter compounds, except in so far as the production of disulphide and sulphite is concerned; for example, in the reaction between sodium ethyl thiosulphate and potassium hydroxide, either in alcoholic or in aqueous solution, no sulphide appears to be formed, but sulphide is formed in both aqueous and alcoholic solution with sodium benzyl thiosulphate, although apparently in smaller amount in the latter case. Again, with an alcoholic solution of sodium benzyl thiosulphate, the reaction appears to be further complicated by the production of an appreciable quantity of mercaptan, the odour of this being much more marked than when aqueous solutions are used; this is in accordance with the observation that alcoholic potash does slowly attack dibenzyl disulphide.

We have not further investigated the discrepancy between the quantitative results obtained by Gutmann in alcoholic solution and those obtained by us with aqueous solutions, since Gutmann states that he is continuing his work on the subject. It may possibly be attributable to the following cause. The first step in the action of alkali on sodium alkyl thiosulphates, as previously stated, is probably represented by the equation :



In alcoholic solution the sulphite, being insoluble, separates out as soon as it is formed, and is thus not further oxidised to sulphate. The oxygen from the three hydroxyl groups may then be absorbed by sodium ethoxide, and the RS residues are therefore free to couple together to disulphide without being further affected. On the other

* At the end of his paper, Gutmann mentions that he intends to investigate further the action of arsenite, cyanide, &c., on disulphides, but it was necessary for us to perform the above qualitative tests to make our work complete. We have not tested his quantitative results.

hand, in aqueous solution, the sulphite is partly oxidised to sulphate, and at the same time the oxygen liberated from the hydroxyl groups attacks some of the RS residues.

That this explanation is a feasible one is borne out by the fact that the presence of a good reducing agent, such as sodium hyposulphite, affects the action of sodium hydroxide on sodium benzyl thiosulphate, causing the separated disulphide to be practically colourless, and at the same time increasing the yield.

EXPERIMENTAL.

Sodium Ethyl Thiosulphate and Alkali.

A mixture of 15 grams of ethyl iodide, 40 c.c. of 90 per cent. alcohol, 30 grams of sodium thiosulphate, and 30 c.c. of water, was heated for an hour on the water-bath, using a reflux condenser. To the homogeneous solution, which now contained sodium ethyl thiosulphate, was added a solution of 15 grams of potassium hydroxide in 30 c.c. of water, and the mixture re-heated for a quarter of an hour. The oil which separated was extracted with ether, and, after distilling off the latter, 2.6 grams of diethyl disulphide, boiling at $150-151^{\circ}$, were obtained. This constitutes a 44 per cent. yield, but some of the disulphide was obviously lost by distilling over with alcohol below the correct boiling point. The disulphide was fully identified by its odour, boiling point, and formation of the characteristic additive compound with silver nitrate.

Sodium Benzyl Thiosulphate and Alkali.

A known weight of sodium benzyl thiosulphate was dissolved in water, 25 c.c. of a potassium hydroxide solution of known strength (approx. 3*N*) added, and the mixture heated on a water-bath in an atmosphere of hydrogen for two hours. The separated disulphide was filtered off, dried, and weighed. The filtrate was diluted to 250 c.c., and an aliquot portion treated with cadmium carbonate in order to remove the sulphide. The sulphur thus removed was converted into barium sulphate, the weight of which gave the amount of sulphur as sulphide (and as thiobenzoic acid).*

The sulphite was estimated in the filtrate from the cadmium carbonate by titration with iodine, whilst the sulphite and sulphate were estimated in part of the same solution by oxidation with bromine

* From the fact that in the analysis the whole of the sulphur is accounted for by the sulphide, sulphite, sulphate, and dibenzyl disulphide, it is probable that the thiobenzoic acid yields its sulphur to the alkaline emulsion of cadmium carbonate, its sulphur, therefore, being included in the number for the sulphide.

water and precipitation as barium sulphate (compare Gytman, *Zeitsch. anal. Chem.*, 1907, 46, 485).

Benzyl sodium thio- sulphate taken.	KOH used.	Sulphite formed.	Sulphate formed.	Sulphide (+ thio- benzoic acid) formed.	Dibenzyl disulphide formed.
I. 0.0257 that is 3.0	0.0343 4.0	0.0238 2.78	0.0063 0.78	0.0067 0.79	0.00813 mols. 0.95 "
II. 0.0271 that is 3.0	0.0363 4.0	0.0252 2.80	0.0043 0.47	0.00745 0.83	0.00894 " 1.0 "

In each experiment the number of atoms of sulphur contained in the sodium benzyl thiosulphate taken was six; in the first experiment the number of atoms of sulphur found as sulphite, sulphate, sulphide, and disulphide is $6.25(=2.78+0.78+0.79+2 \times 0.95)$, and in the second experiment, $6.10(=2.80+0.47+0.83+2 \times 1.0)$, which is a satisfactory agreement for measurements of this kind.

In an experiment in which sodium carbonate was used instead of potassium hydroxide, 3 grams (3 mols.) of sodium benzyl thiosulphate gave 1.10 grams (1.01 mols.) of disulphide.

The presence of thiobenzoic acid in the solution from the action of caustic alkali was proved by acidifying and extracting the oily precipitate with ether. The residue from the ethereal extract consisted of benzoic and thiobenzoic acids. The latter was identified by preparing a solution of the sodium salt, which gave a greenish-yellow precipitate, turning red on standing, with a solution of copper sulphate. A more satisfactory test for the thiobenzoic acid was the formation of benzoyl disulphide, $(C_6H_5 \cdot CO)_2S_2$, by oxidation (compare Fromm and Schmoldt, *Ber.*, 1908, 40, 2861). A solution of potassium ferricyanide was added to the alkaline solution of the mixture of sodium benzoate and thiobenzoate; after some hours, the benzoyl disulphide was filtered off. After recrystallisation from alcohol, it melted at 128° , becoming purple in colour at the same time.

The benzoic acid was detected in the filtrate from the benzoyl disulphide by acidifying and extracting with ether. The residue from the ethereal extract, after recrystallisation from water, melted at 121° , and responded to the usual tests for benzoic acid. No attempt was made to estimate the amounts of benzoyl disulphide and benzoic acid; the quantities obtained were only small.

Part of the expense of the foregoing investigations was defrayed by a grant awarded by the Committee of the Research Fund, for which we wish to express our thanks.

MUNICIPAL TECHNICAL SCHOOL,
BIRMINGHAM.

CXXXV.—*The Preparation of Disulphides. Part-III.*
The Nitrobenzyl Disulphides.

By THOMAS SLATER PRICE and DOUGLAS FRANK TWISS.

IN a previous paper (Trans., 1907, 91, 2021) a method has been described for the preparation of dibenzyl and diethyl disulphides by the electrolysis of the corresponding sodium alkyl thiosulphates in neutral or in alkaline solution. While endeavouring to extend this method to the various nitrobenzyl disulphides, a solution of sodium *p*-nitrobenzyl thiosulphate was rendered alkaline by the addition of sodium carbonate, with the unexpected result, however, that a precipitate began immediately to separate out slowly. This did not occur when sodium hydrogen carbonate was used in place of the normal carbonate, and the electrolysis of this solution gave a brown, sandy deposit, which became gradually paler in colour on repeated recrystallisation from alcohol. Later work showed that this deposit was probably impure *p*-nitrobenzyl disulphide. Even when carbon dioxide was passed into the solution during electrolysis, the deposited solid was strongly coloured. Electrolysis in a solution acidified with sulphuric acid gave no definite result, possibly because the formation of disulphide depends on the reduction of the complex thiosulphate ion, which is not present to any great extent in sulphuric acid solution.

Electrolysis of a solution of sodium *m*-nitrobenzyl thiosulphate containing sodium hydrogen carbonate (sodium carbonate again caused the formation of a precipitate) gave a pasty mass, which appeared to be a very impure *m*-nitrobenzyl disulphide.

In the electrolysis of a solution of sodium *o*-nitrobenzyl thiosulphate to which sodium hydrogen carbonate had been added (sodium carbonate could not be used for the same reason as above), only a small quantity of an oil was obtained, which, from its odour, contained some *o*-nitrobenzyl mercaptan; there was no solid formed. The resistance to reduction, and the formation of mercaptan instead of disulphide, is possibly due to the nitro-groups in the ortho-position offering steric hindrance to the coupling of the two $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{S}$ -residues.

Although the electrolysis of the sodium nitrobenzyl thiosulphates offered little promise as a method for preparing the corresponding disulphides, a successful method of preparation was immediately forthcoming. An examination of the solid produced by the interaction of sodium *p*-nitrobenzyl thiosulphate and sodium carbonate in

solution, showed that it ~~was the required disulphide~~; moreover, not only could the reaction be applied to the *m*- and *o*-nitrobenzyl thiosulphates as well, but it held also for other complex thiosulphates, such as sodium ethyl thiosulphate and sodium benzyl thiosulphate. The formation of diethyl and dibenzyl disulphides in this manner is described in the preceding paper.

In the preparation of *p*-nitrobenzyl disulphide by this method, sodium hydroxide cannot be used, since the disulphide is very sensitive to caustic alkali, giving a deep brownish-red substance, of at present unknown constitution; but in the cold, sodium carbonate causes the slow precipitation of a creamy-white mass of the disulphide. It is not necessary to isolate the sodium *p*-nitrobenzyl thiosulphate, since the solution obtained by boiling together *p*-nitrobenzyl chloride and sodium thiosulphate in aqueous alcoholic solution may be used. The yield amounts to about 60 per cent. of that theoretically expected from the nitrobenzyl chloride taken, so that the reaction is probably similar to that with sodium benzyl thiosulphate and alkalis (*loc. cit.*). Even in the absence of alkali, solutions of sodium *p*-nitrobenzyl thiosulphate very slowly deposit the disulphide.

In a similar way, *m*-nitrobenzyl disulphide has been obtained from a solution of sodium *m*-nitrobenzyl thiosulphate. The use of sodium hydroxide causes the precipitated disulphide to be somewhat pink in colour, whilst sodium carbonate gives a white solid, which is practically pure. The reaction with sodium carbonate is slow at the ordinary temperature, being unfinished even after a fortnight, but the product is much less pure if heating is resorted to.

Similarly, *o*-nitrobenzyl disulphide has been obtained from solutions of sodium *o*-nitrobenzyl thiosulphate. As with the meta-compound, the reaction proceeds very slowly. Sodium hydroxide causes a more rapid precipitation than does the carbonate, but the separated disulphide then has a tendency to pastiness and is less pure. The yield is poor in both cases, sodium carbonate after several days giving a yield of 25 per cent. calculated on the nitrobenzyl chloride taken; this yield is poorer than that of either of the corresponding meta- or para-compounds. Warming the mixture does not hasten the precipitation, but gives a strong odour of the *o*-nitrobenzyl mercaptan, confirming the idea that the nitro-group in the ortho-position causes steric hindrance to the formation of disulphide.

It will thus be seen that although the nitrobenzyl thiosulphate compounds do not behave towards electrolysis in the same way as the unsubstituted sodium benzyl thiosulphate, they yet follow a general reaction of these organic thiosulphates with solutions of alkalis.

The three disulphides obtained in the course of this investigation have not been isolated before, the *o*-nitrobenzyl disulphide of Jahoda (*Monatsh.*, 1890, 10, 874) having been proved to be in reality the corresponding mercaptan (Gabriel and Stelgner, *Ber.*, 1896, 29, 161). The melting points of these three disulphides stand in the order: para, 126.5°; ortho, 109.5°; meta, 103°.

During this investigation, the three sodium nitrobenzyl thio-sulphates have been isolated; they are all crystalline substances, the meta-compound having a faint green fluorescence.

EXPERIMENTAL.

Sodium p-nitrobenzyl thiosulphate, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{S}_2\text{O}_3\text{Na}$, is readily obtained by boiling together 20 grams of *p* nitrobenzyl chloride with 30 grams of sodium thiosulphate in 60 c.c. of alcohol and 60 c.c. of water for one hour. The liquid, on cooling, deposits crystals of the sodium *p*-nitrobenzyl thiosulphate, which can be purified by recrystallisation from alcohol. A further quantity can be obtained from the original mother liquor by evaporation to dryness and extraction with alcohol:

0.4532 gave 0.1174 Na_2SO_4 . $\text{Na} = 8.39$.

$\text{C}_7\text{H}_6\text{O}_3\text{NS}_2\text{Na}$ requires $\text{Na} = 8.48$ per cent.

p-Nitrobenzyl disulphide, $(\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2)_2\text{S}_2$, is prepared by the action of sodium carbonate on sodium *p*-nitrobenzyl thiosulphate. Experiments were performed to find the best conditions for the formation of disulphide. In each case a solution of sodium carbonate containing 30 grams of the crystallised salt in 60 c.c. of water was used.

Weight of Na <i>p</i> -nitro- benzyl thiosulphate, grams.	Water, c.c.	Sodium carbonate solution, c.c.	Weight of disulphide, gram.
2	10	1	0.70
2	10	16	0.70
2	40	1	0.76
2	40	39	0.72

Within the above limits, alterations in concentration do not seem to have much effect. The highest yield is approximately 60 per cent. on the thiosulphate compound taken, showing the reaction to be similar to that with sodium benzyl thiosulphate (*loc. cit.*). A solution of pure sodium *p*-nitrobenzyl thiosulphate slowly deposits the disulphide, but even after months the amount formed is very small.

If a solution of sodium hydroxide be used instead of sodium carbonate, there is an immediate brownish-red precipitate of very

impure disulphide, the colour being due to the further action of the alkali on part of the disulphide formed.

It is not necessary to isolate the thiosulphate compound in order to prepare the disulphide. Instead of allowing the product of the interaction of nitrobenzyl chloride and sodium thiosulphate to crystallise, an equal bulk of water is added, and then, when cold, a fairly dilute aqueous solution of sodium carbonate, containing approximately the same weight of crystallised sodium carbonate as of nitrobenzyl chloride originally taken. After standing for one or two days the creamy white precipitate of disulphide is collected, washed with water, then with dilute acid to remove alkali, towards which the disulphide is so sensitive, and again with water. After recrystallisation twice from alcohol it is pure, and is then obtained in pale yellow needles, melting at 126.5° . It is fairly soluble in hot alcohol, but very soluble in pyridine. Its solution in alcohol gives a deep blood-red coloration when mixed with alcoholic potash :

0.2988 gave 0.4160 BaSO_4 . $S = 19.12$.

$\text{C}_{14}\text{H}_{13}\text{O}_4\text{N}_2\text{S}_2$ requires $S = 19.05$ per cent.

Sodium m-nitrobenzyl thiosulphate is prepared in exactly the same manner as the para-compound, using *m*-nitrobenzyl chloride. It is a pale yellow solid with a faint green fluorescence. Although recrystallised from 90 per cent. alcohol it apparently contains water of crystallisation :

0.8265 gave 0.2055 Na_2SO_4 . $\text{Na} = 8.06$.

After recrystallisation 0.3720 gave 0.0919 Na_2SO_4 . $\text{Na} = 8.00$.

After another recrystallisation 0.4240 gave 0.1048 Na_2SO_4 . $\text{Na} = 8.01$.

$\text{C}_7\text{H}_6\text{O}_3\text{NS}_2\text{Na} \cdot \text{H}_2\text{O}$ requires $\text{Na} = 7.96$ per cent.

m-Nitrobenzyl disulphide. A mixture of 10 grams of *m*-nitrobenzyl chloride, 20 grams of sodium thiosulphate in 40 c.c. alcohol and 40 c.c. of water was heated under reflux for one hour; the resulting solution was diluted with an equal bulk of water, and after the addition of 15 grams of crystallised sodium carbonate dissolved in 30 c.c. water, was allowed to stand. The precipitation of disulphide took place slowly in the cold, but became more rapid on warming to about 60° ; heating more strongly caused the separated disulphide to be pinkish in colour, owing to contamination with impurities. The disulphide formed from the cold solution was pure after one recrystallisation from alcohol. It forms pale yellow crystals, melting at 103° :

0.2982 gave 0.4131 BaSO_4 . $S = 19.05$.

0.2920 „ 0.4066 BaSO_4 . $S = 19.12$.

$\text{C}_{11}\text{H}_{10}\text{O}_4\text{N}_2\text{S}_2$ requires $S = 19.05$ per cent.

Sodium o-nitrobenzyl thiosulphate was prepared in a similar manner.

to the para- and meta-compounds. It is a pale yellow, crystalline solid:

* 0.2015 gave 0.0521 Na_2SO_4 . $\text{Na} = 8.37$.

$\text{C}_7\text{H}_6\text{O}_5\text{NS}_2\text{Na}$ requires $\text{Na} = 8.48$ per cent.

o-Nitrobenzyl disulphide. A solution of the thiosulphate compound was treated with sodium carbonate solution, the process being exactly the same as described for the preparation of the meta-compound. The *o*-nitrobenzyl disulphide separated out slowly for several days. The product was collected, washed with water, then with dilute acid, and finally with water. It was purified by recrystallisation from alcohol, and was then obtained in pale yellow crystals melting at 109.5° :

0.1735 gave 0.2437 BaSO_4 . $\text{S} = 19.28$.

$\text{C}_{14}\text{H}_{12}\text{O}_4\text{N}_2\text{S}_2$ requires $\text{S} = 19.05$ per cent.

Part of the expense of the foregoing investigation was defrayed by a grant awarded by the Committee of the Research Fund, for which we wish to express our thanks. The research is being continued.

CHEMICAL DEPARTMENT,
MUNICIPAL TECHNICAL SCHOOL,
BIRMINGHAM.

CXXXVI.—*Solubility of Silver Chloride in Mercuric Nitrate Solution.*

By BERTRAM HAWARD BUTTLE and JOHN THEODORE HEWITT.

ABOUT a year ago a short note was communicated by one of the present authors (Proc., 1907, 23, 10) describing the isolation of a basic mercuric chloride, $\text{Hg}_6\text{O}_5\text{Cl}_2$, which apparently had not previously been observed. Some difficulty was at first experienced in carrying out the analysis, since it was found that a solution of the substance in dilute nitric acid gave no precipitate with medium amounts of silver nitrate solution; indeed, it was at first supposed that the substance possessed the formula $\text{Hg}_2\text{O}(\text{OH})_2$, which requires 88.88 per cent. of mercury, whilst $\text{Hg}_6\text{O}_5\text{Cl}_2$ requires 88.82 per cent., two estimations having given 88.53 and 88.65 per cent. respectively. The fact that the compound suffered no appreciable loss of weight on prolonged heating at 110° made it necessary to look for a further cause than the presence of hydroxide water for the low percentage of mercury (HgO requires $\text{Hg} = 92.59$ per cent.), and a few experiments

of a qualitative nature soon showed that silver chloride is readily dissolved by a solution of mercuric nitrate containing free nitric acid.

As a result of this observation, numerous measurements of the solubility of silver chloride in mercuric nitrate solutions were carried out, and only when the experimental work was practically completed the authors became aware of the fact that measurements of a similar nature had been executed by H. Morse in the Leipzig laboratory with the object of determining the dissociation constant of mercuric chloride (*Zeitsch. physikal. Chem.*, 1902, 41, 709).

Despite this fact, it may be worth while to record the new observations, since different concentrations have been employed and the influence of varying amounts of nitric acid has been studied. In calculating the dissociation constant of the mercury-chlorine complex contained in the solution, a different method has been adopted, the constant so determined, whilst of the same order as that given by Morse, being appreciably greater in magnitude.

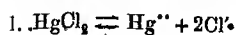
One of the first observations relating to mercury salts and silver halides is due to Gay Lussac, who noticed that the former hindered the titration of chlorine by means of silver nitrate. Wackenroder (*Annalen*, 1842, 41, 317) observed that the silver halides dissolve comparatively easily in mercuric nitrate solutions, and Stas (*Ann. Chim. Phys.*, 1874, [v], 3, 179) made a few estimations of these solubilities. The fundamental cause only became apparent on the acceptance of the theory of ionic dissociation; the solubility of silver chloride in water is such that one may assume a practically complete dissociation of the silver chloride, but if ions capable of discharging the chlorine ions be added to the solution, more silver chloride will dissolve in order to preserve the constancy of the solubility product for this salt. This was recognised by Luther (*Zeitsch. physikal. Chem.*, 1901, 36, 402), who suggested that the extent of the ionisation of the mercuric chloride could be determined by measurement of the solubility of silver chloride in mercuric nitrate solution, for, since the solubility product of silver chloride is known, one immediately obtains a measure of the concentration of the chlorine ions, silver salts being almost completely ionised in fairly dilute solutions.

The concentration of the mercury ions is not such a simple matter to evaluate, as one is left in some uncertainty as to the extent to which the mercuric nitrate is ionised. Morse (*Zeitsch. physikal. Chem.*, 1902, 41, 709) obtained an approximate value by finding the lowering of freezing point of normal and decinormal solutions of nitric acid by corresponding amounts of mercuric nitrate, and concluded that in both cases about 0.4 of the mercuric nitrate present was ionised to mercurions, Hg^{++} . With the values obtained for the concentration of the mercury and chlorine ions, Morse was enabled to test which of the

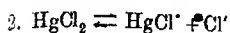
onic reactions represented by the equilibrium equations in the first column was chiefly responsible for the removal of the chlorine ions and consequent solution of the silver chloride:

Equilibria.

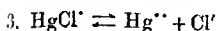
Corresponding Constants.



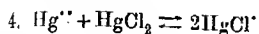
$$\frac{[\text{Hg}^{++}] \times [\text{Cl}']^2}{[\text{HgCl}_2]} = K_1$$



$$\frac{[\text{HgCl}'] \times [\text{Cl}']}{[\text{HgCl}_2]} = K_2$$



$$\frac{[\text{Hg}^{++}] \times [\text{Cl}']}{[\text{HgCl}']} = \frac{K_1}{K_2} = K_3$$

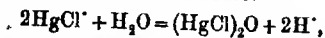


$$\frac{[\text{Hg}^{++}] \times [\text{HgCl}_2]}{[\text{HgCl}']^2} = \frac{K_1}{K_2^2} = K_4$$

Morse's procedure consisted in either digesting a known weight of silver chloride with mercuric nitrate solution containing free nitric acid and weighing the excess of undissolved material, or else solutions containing known amounts of silver nitrate, mercuric chloride, and mercuric nitrate were shaken together and the amount of silver chloride which separated was estimated. Out of five series of experiments, four gave a fair constancy of K_3 , whilst in the set where the amount of mercuric chloride was varied and considerable quantities of this salt were employed, satisfactory values were not obtained. In this case, much of the mercuric chloride was quite undissociated, but by means of partition coefficient experiments on this salt, using toluene and water and toluene and mercuric nitrate solution as solvents, values were obtained for K_2 and K_4 , and then, on applying the necessary correction, the results came fairly into line with those obtained in the other series.

Morse concludes that where the excess of mercuric nitrate is considerable, the chlorine is almost entirely present in the form of HgCl' ions, but that when the amount of mercuric chloride is increased relatively to the mercuric nitrate, a considerable amount of the former is present in an undissociated condition.

Subsequently, Sherrill (*Zeitsch. physikal. Chem.*, 1903, **43**, 705) published measurements of the extent to which complex ion formation takes place; the interpretation of the results afterwards underwent revision by this author, who had overlooked Morse's paper (*ibid.*, 1904, **47**, 103), and Luther utilised the results which had been obtained (*ibid.*, **47**, 107) to estimate the extent to which solutions of mercuric chloride are hydrolysed. This aspect of the case had previously occupied the attention of Ley (*Ber.*, 1897, **30**, 2192; *Zeitsch. physikal. Chem.*, 1899, **30**, 247). Luther considers that the hydrolysis occurring in a mercuric chloride solution takes the course



and estimates that undissociated mercuric chloride and various ions

are present in a saturated solution of this salt at 25° in the following amounts expressed in mols. per litre:

HgCl ₂	2.6×10^{-1}	HgCl [•]	1.5×10^{-4}
H ⁺	3.3×10^{-4}	Hg ^{••}	1.0×10^{-4}
Hg ₂ Cl ₂ O	1.7×10^{-4}	HgCl ₂ ^{••}	5.0×10^{-6}
Cl ⁻	4.3×10^{-4}		

In our experiments, we studied the effect of known amounts of nitric acid on the solubility of silver chloride in mercuric nitrate, and found that the more the acid was increased, so much less of the halide was dissolved. The decrease was, however, small, and, if we consider the equilibria likely to be established in solutions strongly acidified with nitric acid, the result seems fairly easy of explanation:

- (a) $\text{Hg}(\text{NO}_3)_2 \rightleftharpoons \text{Hg}(\text{NO}_3)^+ + (\text{NO}_3)^- \rightleftharpoons \text{Hg}^{++} + 2(\text{NO}_3)^-$.
- (b) $\text{AgNO}_3 \rightleftharpoons \text{Ag}^+ + (\text{NO}_3)^-$.
- (c) $\text{Hg}^{++} + \text{Cl}^- \rightleftharpoons \text{HgCl}^+$.
- (d) $\text{Hg}(\text{NO}_3)^+ + \text{Cl}^- \rightleftharpoons \text{Hg}(\text{NO}_3)\text{Cl} \rightleftharpoons \text{HgCl}^+ + (\text{NO}_3)^-$.
- (e) $\text{Ag}^+ + \text{Cl}^- \rightleftharpoons \text{AgCl}$ (precipitated).

Addition of nitric acid will have a double effect, in that it will diminish the dissociation of both the mercuric and silver nitrates. The first effect (a) would result in a greater precipitation of silver chloride, the mercury salt being less active in removing chlorine ions. The second effect (b) would necessitate less silver chloride being precipitated, the concentration of the silver ions being diminished. The two effects thus partly neutralise one another, the effect due to decrease in the ionisation of mercuric nitrate somewhat outweighing that due to the decrease in the ionisation of the silver nitrate (see table IV).

Another effect of the nitric acid will be to diminish the hydrolysis of the mercuric nitrate. In none of our experiments can this hydrolysis be sufficient to affect the results appreciably, for we have taken three equivalents of nitric acid as a minimum for the solution of one equivalent of mercuric oxide.

Two corresponding sets of experiments were carried out in which the amounts of mercuric nitrate and nitric acid were kept constant, and either the amount of silver nitrate was increased whilst the hydrochloric acid was kept constant, or the latter was varied whilst the same amounts of silver nitrate were taken. The results showed that practically the same amount of precipitate was produced under these conditions by x molecules of hydrochloric acid and y molecules of silver nitrate, or by x molecules of the latter and y of the former. Since each molecule of silver nitrate gives only one silver ion, the molecules or ions from which the chlorine ions are supplied must evidently furnish one such ion apiece. If they arose directly from

the added hydrochloric acid, no further comment would be necessary, since one molecule of hydrochloric acid of necessity furnishes one chlorine ion. But, as we know, the ionised hydrochloric acid and mercuric nitrate interact with formation of a complex from which but few chlorine ions are produced, and if n chlorine ions were used in producing one of these complexes and one chlorine atom were more readily set free as an ion from this complex than the remaining $n - 1$, it is evident that the addition of equivalent amounts of hydrochloric acid and the strongly ionised silver nitrate could not be equally efficacious in the precipitation of silver chloride. This argument would not hold if all the n chlorine atoms of the complex (ion or salt) were split off with equal readiness; this, however, would be out of the question even if the work of Morse and Luther, which shows that the dissociation constants for the two chlorine atoms of mercuric chloride have different values, had not been carried out. We thus arrive at the same general conclusion as Morse: "Falls wir Merkurinitrat in grossem Ueberschusse haben, ist Chlor fast nur in Form von HgCl^+ ion vorhanden"; and even with quite a moderate excess of mercuric nitrate, so small is the ionisation of the HgCl^+ complex that we may safely put its concentration equal to that of the chlorine remaining in the solution.

The variation in the solubility of silver chloride in solutions of mercuric nitrate with proportionate amounts of free nitric acid has also been studied; the results are given in table V and are used for the determination of the constant

$$K_3 = \frac{[\text{Hg}^{++}] \times [\text{Cl}^-]}{[\text{HgCl}^+]},$$

which we find to be 5.3×10^{-8} , whilst Morse gives the value 3.5×10^{-8} .

EXPERIMENTAL.

Reagents Employed.—The water used in these experiments was distilled from a tinned-iron vessel, condensed in glass, and stored in a tubulated glass bottle; both condenser and bottle have been used exclusively for this purpose for some years past. The water was not of the degree of purity that would be employed for conductivity experiments, but showed no traces of iron, sulphates, or chlorides.

The nitric acid was prepared from commercially pure nitric acid (sp. gr. 1.42), which, after slight dilution and addition of silver nitrate and cyanamide, was distilled from apparatus entirely of glass with asbestos luting. The first fractions were rejected, and all specimens were quite colourless.

The hydrochloric acid (commercial pure fuming) was diluted with rather more than its own weight of water and redistilled, the first fraction again being rejected.

* Both acids were diluted, the nitric acid to just over 2*N* or 5*N*, and the hydrochloric acid to slightly above 2*N*, and the strength accurately determined by means of standard baryta.

The mercuric nitrate solutions were made by dissolving weighed amounts of mercuric oxide (precipitated by potassium hydroxide from mercuric chloride, thoroughly washed, and dried, first, at 130° and then over sulphuric acid for a fortnight) in known quantities of pure nitric acid.

The silver nitrate was a pure commercial sample.

Experimental Procedure.—In studying the reaction between chloride and silver nitrate in presence of mercuric nitrate, the following procedure was adopted: Solutions of mercuric nitrate, silver nitrate, and hydrogen chloride, all of known strength, were taken in the requisite proportions, the volume made to 100 c.c. with distilled water, and the solution and precipitate gently agitated in a thermostat at 25° for five hours. The precipitate being finely divided to begin with, the time mentioned was found to be ample for the establishment of equilibrium; in tables II, IV, and V several cases are given where the experiments have been executed in duplicate or triplicate; the concordance of the results in these cases points plainly to the reliability of the experimental results. The temperature-coefficient of the solubility of silver chloride in mercuric nitrate being considerable, a fair sized thermostat in which the temperature could be maintained for several hours between 24.97° and 25.05° was employed.

To estimate the silver chloride which had been precipitated, the liquid was rapidly filtered through an Allihn tube closed with platinum gauze and a plug of washed asbestos, the precipitate washed successively with dilute nitric acid and water, the tube and its contents dried, weighed, and roasted in a current of hydrogen to a constant weight. In calculating the results, it was found that better concordance was obtained by using the weights of silver than of silver chloride, for a small amount of mercury salts is always retained by the asbestos and prolonged washing is dangerous on account of the solubility of the silver chloride.

It was necessary to show, however, that the precipitate produced in these solutions actually consisted of silver chloride, and did not contain appreciable amounts of a silver mercurichloride (or mercurinitrate). A number of experiments were accordingly made in which the limit of the concentrations covered those of the different reagents subsequently employed; the precipitates were collected in Gooch crucibles but not washed, as decomposition of double salts might ensue. After drying, a portion of each precipitate was reduced in a current of hydrogen and the resulting silver weighed. The percentage of silver necessarily falls in each case below the theoretical for silver chloride.

(75.28), but the results leave no doubt as to the absence of double salts in the precipitate (Ag_2HgCl_4 requires $\text{Ag}=38.70$ per cent.).

In each case (table I), the total volume was 100 c.c.; the weights of nitric acid in the second column give the total nitric acid used to dissolve the mercuric oxide, of which the weight is recorded in the first column.

TABLE I.

Weight (in grams) of substances taken.				Analysis of residues.		
HgO .	HNO_3 .	HCl .	AgNO_3 .	Precipitate reduced.	Ag found.	Ag per cent.
1.08	1.8906	0.0365	0.1699	0.0309	0.0231	74.75
1.08	1.8906	0.0729	0.1699	0.0871	0.0652	74.86
1.08	1.8906	0.0365	0.3398	0.0847	0.0633	74.73
1.08	1.8906	0.0911	0.4248	0.2133	0.1572	74.05
5.40	9.4530	0.0911	0.1248	0.0835	0.0617	73.89
5.40	9.4530	0.0911	1.3595	0.2211	0.1648	74.54
5.40	9.4530	0.3646	0.4248	0.2322	0.1734	74.68
2.70	4.7265	0.2279	0.4248	0.2688	0.2012	74.85
2.70	4.7265	0.0911	1.3595	0.2814	0.2106	74.84
1.08	1.8906	0.2279	0.4248	0.3023	0.2268	75.02
1.08	1.8906	0.0911	0.8497	0.2751	0.2066	75.10

As pointed out in the introduction, addition of equimolecular proportions of hydrogen chloride or silver nitrate promote the precipitation of silver chloride to practically the same extent if the other components are kept constant in amount. In table II the effect of adding increasing amounts of hydrochloric acid is recorded; in each case, 100 c.c. contained 1.08 grams of mercuric oxide, 1.8906 grams of nitric acid, and 0.4248 gram of silver nitrate ($=0.2698$ gram Ag). Assuming that one molecule of mercuric oxide combines with two molecules of nitric acid, we should have a concentration of 0.05 mercuric nitrate, 0.025 silver nitrate, and 0.20 free nitric acid (all expressed in gram-molecules per litre) were it not for the precipitation of silver chloride.

TABLE II.

HCl added.		Ag precipitated as AgCl (in grams).	Ag remaining in solution.	
Gram per 100 c.c.	Mols. per litre.		Gram per 100 c.c.	Gram-atoms per litre.
0.0911	0.025	0.1703	Mean 0.0998	0.00924
0.0911	0.025	0.1696		
0.1094	0.03	0.1943	0.0755	0.00699
0.1458	0.04	0.2195	0.0503	0.00466
0.1823	0.05	0.2347	0.0351	0.00325
0.2279	0.0625	0.2447	0.0251	0.00232
0.2917	0.08	0.2532	0.0166	0.00154

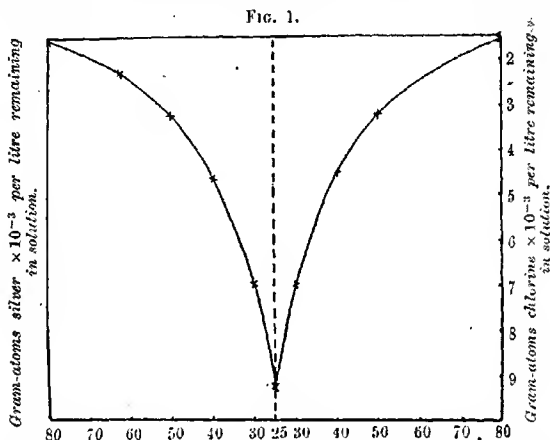
In table III the results are recorded starting with 1.08 grams of mercuric oxide, 1.8906 grams of nitric acid, 0.0911 gram of hydrochloric acid, and varying the amount of silver nitrate in the solution, the total volume as in the last set of experiments being 100 c.c.

TABLE III.

AgNO ₃ added.		Cl (in grams) precipitated as AgCl	Cl remaining in solution.	
Grams per 100 c.c.	Mols. per litre.		Gram per 100 c.c.	Gram-atoms per litre.
0.4248	0.025	0.0557	0.0329	0.00924
0.5098	0.030	0.0640	0.0246	0.00697
0.6798	0.040	0.0726	0.0160	0.00451
0.8497	0.050	0.0772	0.0114	0.00322
1.3595	0.080	0.0831	0.0055	0.00156

The results of these two series of experiments are plotted in Fig. 1.

The symmetry of the curves leaves little doubt that the complex furnishing the chlorine ions contains but one chlorine atom per com-



AgNO₃ constant = 0.025 mols. per litre. | HCl constant = 0.025 mols. per litre.
HCl variable. Mols. $\times 10^{-3}$ per litre. | AgNO₃ variable. Mols. $\times 10^{-3}$ per litre.

plex. The result is interesting as confirming Morse's conclusion from a different point of view.

Before proceeding to the results which lead to a value for the dissociation constant

$$\frac{[\text{Hg}^{++}] \times [\text{Cl}^-]}{[\text{HgCl}^+]}$$

the effect of varying amounts of nitric acid on the solubility of silver chloride in mercuric nitrate has to be noted (table IV).

In each case, 100 c.c. contained 1.08 grams of mercuric oxide, 0.0911 gram of hydrochloric acid, and 0.4248 gram of silver nitrate, the mercuric oxide having been dissolved in the amount of nitric acid given in the first and second columns.

TABLE IV.

HNO ₃ total.			As remaining in solution.	
Gram per 100 c.c.	Mols. per litre.	Ag (in grams) pre- cipitated as AgCl.	Gram per 100 c.c.	Gram-atoms per litre.
1.8906	0.30	0.1700	0.0998	0.00924
2.5208	0.40	0.1726	0.0972	0.00901
3.1510	0.50	0.1750	0.0948	0.00878
3.7812	0.60	0.1757	0.0941	0.00872
3.7812	0.60	0.1756		
4.4214	0.70	0.1770		
4.4214	0.70	0.1765	0.0930	0.00862

That increase in nitric acid content should slightly increase the precipitation of the silver chloride has been already mentioned, and the results, although somewhat irregular, certainly bear out the conclusion derived from theoretical considerations. The statement made by Morse that in his experiments four-tenths of the mercuric nitrate may be taken as dissociated, must be regarded as a near approximation; in fact, he says, the value may be affected with an error of 10 per cent. to 20 per cent. It is evident from general considerations that normal mercuric nitrate in normal nitric acid must be dissociated to a less extent than when the two substances are both decinormal in concentration.

In estimating the dissociation constant of the HgCl^+ ion, we have employed a radically different method of finding its value. The concentration of the chlorine ion in the solution is given by the expression

$$[\text{Ag}^+] \times [\text{Cl}^-] = P^2,$$

where P^2 is the solubility product of silver chloride; this, like Morse, we have taken as $(1.35 \times 10^{-5})^2$ at 25°. Now this concentration of the chlorine ion is of a low order, consequently we may take the concentration of mercuric nitrate (ionised or non-ionised) as equal to the total concentration of the mercuric salt diminished by the concentration of the chlorine, which latter is necessarily identical with the concentration of the silver in the solution if equivalent quantities of hydrogen chloride and silver nitrate have been used. The silver can be assumed to be entirely in the ionic condition at the dilutions employed without introducing any sensible error (compare Löb and Nernst, *Zeitsch. physikal. Chem.*, 1888, 2, 948).

We thus have

$$[\text{Ag}^+] \times [\text{Cl}^-] = P^2 = (1.35 \times 10^{-5})^2 \quad \dots \dots \dots (1)$$

$$[\text{HgCl}^+] = [\text{Ag}^+] - [\text{Cl}^-] = [\text{Ag}^+] \quad \dots \dots \dots (2),$$

* For the solubility of silver chloride, see Hollemann (*Zeitsch. physikal. Chem.*, 1893, 12, 125); Kohlrausch and Rose (*ibid.*, 12, 234); Kohlrausch (*ibid.*, 1903, 44, 197); Buttger (*ibid.*, 1903, 46, 521; 1906, 56, 83).

since the concentration of chlorine ions is negligible compared with that of silver.

Also, if i is the factor of dissociation,

$$[\text{Hg}^{++}] = i[\text{Hg}(\text{NO}_3)_2] \quad (3).$$

The quantities in square brackets refer to concentrations expressed as gram-molecules (or gram-ions) per litre.

Now

$$\frac{[\text{Hg}^{++}] \times [\text{Cl}^-]}{[\text{HgCl}^+]} = K_s,$$

and introducing the values for these concentrations given by equations (1), (2), and (3), the expression reduces to

$$K_s = \frac{i \times [\text{Hg}(\text{NO}_3)_2]}{[\text{Ag}^+]\{[\text{Ag}^+] - [\text{Cl}^-]\}} \times P^2 = iyP^2,$$

where

$$y = \frac{[\text{Hg}(\text{NO}_3)_2]}{[\text{Ag}^+]\{[\text{Ag}^+] - [\text{Cl}^-]\}}.$$

This expression gives a ready means of determining whether i is approximately constant. In table V, the numbers refer to solutions to which had been added 0.0911 gram of hydrogen chloride and 0.4248 gram of silver nitrate per 100 c.c., that is, would have been 0.025*N* with regard to these two constituents if no precipitation had taken place. The first two columns give the weight of mercuric oxide per 100 c.c. and total atomic concentration of mercury. The third column is the weight of nitric acid (grams per 100 c.c.) used for solution of the mercuric oxide, and the fourth gives the weight of

TABLE V.

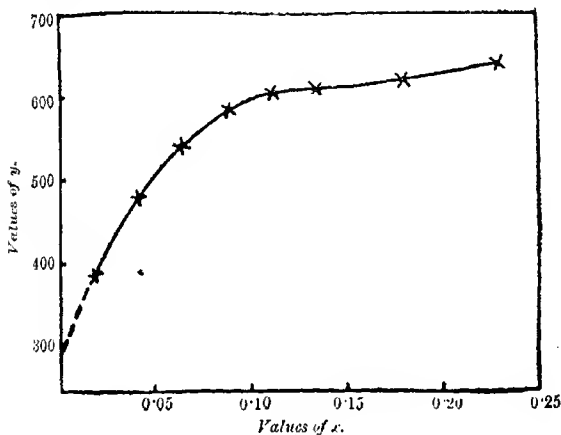
HgO introduced.		HNO ₃		Ag remaining in solution.		$y = \frac{[\text{Hg}(\text{NO}_3)_2]}{[\text{Ag}^+]\{[\text{Ag}^+] - [\text{Cl}^-]\}}$
Grams per 100 c.c.	Mols. per litre = $\frac{[\text{Hg}(\text{NO}_3)_2]}{100}$	used to dissolve HgO.	Weight of Ag (grams per 100 c.c.) contained in AgCl.	Grams per 100 c.c.	[Ag ⁺]	
0.54	0.025	0.9453	0.1965	0.1960	0.00684	383
0.54	0.025	0.9453	0.1954			
0.54	0.025	0.9453	0.1962			
1.08	0.050	1.8906	0.1703	0.1700	0.00924	477
1.08	0.050	1.8906	0.1696			
1.62	0.075	2.8359	0.1524			
1.62	0.075	2.8359	0.1515	0.1521	0.01090	540
1.62	0.075	2.8359	0.1525			
2.16	0.100	3.7812	0.1371	0.1375	0.01226	584
2.16	0.100	3.7812	0.1378			
2.70	0.125	4.7265	0.1239			
2.70	0.125	4.7265	0.1226	0.1233	0.01357	605
2.70	0.125	4.7265	0.1234			
3.24	0.150	5.6718	0.1096	0.1089	0.01490	609
3.24	0.150	5.6718	0.1081			
4.32	0.200	7.5624	0.0846			
5.40	0.250	9.4530	0.0650	0.1852	0.01716	621
				0.2448	0.01897	612

silver in the silver chloride precipitated. The fifth and sixth columns refer to the silver remaining in solution. The seventh column gives the values of the concentrations of mercuric nitrate (corrected for the HgCl') divided by the square of the concentration of silver (y), and this, as we have seen, should be a constant figure if the ionisation factor is itself constant, since P^2 cannot vary. Thus the number in the first horizontal row and seventh column is calculated from the other numbers in this horizontal row in the following manner:

$$\frac{0.02500 - 0.00684}{(0.00684)^2} = 388.$$

It may be pointed out that the mean value of the last column is

FIG. 2.



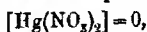
558, and if, following Morse, one assumes a value of $i = 0.4$, then the dissociation of the HgCl' complex should be

$$558 \times (1.35 \times 10^{-5})^2 \times 0.4 = 4.0 \times 10^{-8}.$$

This value agrees fairly closely with the number given by Morse, but obviously cannot be taken as anything more than an approximation, as the figures in the last column are by no means constant.

In Fig. 2 the values of y are plotted against the corrected concentrations of mercuric nitrate, x' (that is, the numbers of column 2 diminished by those of column 6), and, as will be noted, the points lie on a smooth curve.

Now, as the concentrations of mercuric nitrate approach zero, i approaches unity, so that, if we extrapolate for a limiting value when



we shall obtain a limiting value for y , which, multiplied by P^2 , gives the dissociation constant of HgCl^+ .

Using an expression

$$y = a + bx + cx^2 + dx^3$$

and solving for the coefficients with the values of x , given by the first four rows, we obtain

$$a = 292.*$$

Using this value, we have, as a final result,

$$K_2 = \frac{[\text{Hg}^{++}] \times [\text{Cl}^-]}{[\text{HgCl}^+]} = 292 \times (1.35 \times 10^{-5})^2 = 5.3 \times 10^{-8}.$$

This number, it will be noticed, is of the same order of magnitude, but about 50 per cent. greater than that given by Morse.

Further, the values of a/y give a rough estimate of the extent to which the mercuric nitrate is dissociated; with the solution containing the least amount (0.025 mol. per litre), this is 0.75, and with the solution containing 0.1 mol. per litre the value becomes 0.5. With the more concentrated solutions, the effect of the nitric acid in diminishing the ionisation of the mercuric and silver nitrates is probably appreciable, and may account for the form of the curve at the higher concentrations.

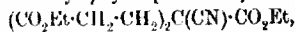
EAST LONDON COLLEGE.

CXXXVII.—*The cis- and trans-Modifications of 1-Methyl-cyclohexan-2-ol-4-carboxylic Acid and their Conversion into 1-Methyl- Δ^1 -cyclohexene-4-carboxylic Acid.*

By ANDREW NORMAN MELDRUM (Carnegie Research Fellow) and WILLIAM HENRY PERKIN, jun.

1-METHYL- Δ^1 -CYCLOHEXENE-4-CARBOXYLIC acid has already been prepared synthetically (Trans., 1904, 85, 418) by the following series of reactions:

Ethyl sodiocyanoacetate is converted by treatment with ethyl β -iodopropionate into ethyl γ -cyanopentane- $\alpha\epsilon$ -tricarboxylate,

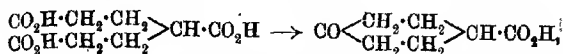


which, when hydrolysed by hydrochloric acid, yields pentane- $\alpha\epsilon$ -tricarboxylic acid.

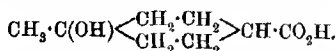
This acid is decomposed by boiling with acetic anhydride and

* $b = 6087$; $c = -43200$; $d = 134500$.

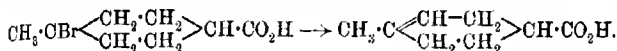
subsequent distillation into *cyclohexanone-4-carboxylic acid* δ -keto-hexahydrobenzoic acid),



the ester of which reacts with magnesium methyl iodide and the product, on treatment with water, yields 1-methylcyclohexan-1-ol-4-carboxylic acid (δ -hydroxyhexahydro-*p*-toluic acid):

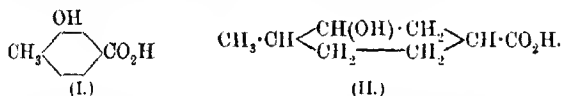


The yield of this acid was always most unsatisfactory, a fact which was subsequently (Trans., 1907, 91, 372) found to be largely due to the formation of considerable quantities of terpin and other neutral substances. The next step in the synthesis was the conversion of the hydroxy-methyl acid into 1-bromo-1-methylcyclohexane-4-carboxylic acid (δ -bromohexahydro-*p*-toluic acid) by the action of hydrobromic acid, and, finally, the bromo-acid, when treated with weak alkalis or pyridine, yielded 1-methyl- Δ^1 -cyclohexene-4-carboxylic acid:



It will be readily understood that this method of preparation is most laborious, and, as the yield is so small, it was found to be practically impossible to obtain this acid, by this process, in quantities sufficient for a further series of synthetical experiments which are in contemplation. We therefore decided to attempt to devise a more convenient method of preparation, and in this we were ultimately successful.

The starting-point is *p*-toluic acid, which is converted by sulphonation into 2-sulpho-*p*-toluic acid, and then by fusion with potassium hydroxide into 2-hydroxy-*p*-toluic acid (I):

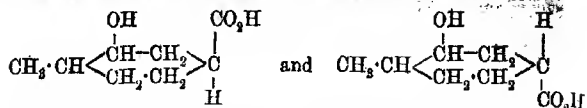


This acid is readily reduced by sodium and alcohol, and converted into the corresponding 1-methylcyclohexan-2-ol-4-carboxylic acid (II).

It is interesting to notice that this addition of six atoms of hydrogen to 2-hydroxy-*p*-toluic acid results in the formation of a hexahydro-acid containing three asymmetrical carbon atoms, which, therefore, should be capable of existing in four inactive modifications.

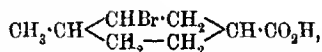
On carefully examining the product of reduction, we were only able, however, to isolate two acids, of melting points 132° and 161°.

respectively, and there can hardly be a doubt that these are the *cis*- and *trans*-modifications corresponding with the formula:

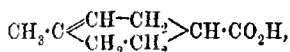


Of these, the more soluble acid melting at 132° is evidently the *cis*-modification, since it yields a lactone (m. p. $30-33^\circ$) which, on hydrolysis, is again converted into the same acid.

On the other hand, the much more sparingly soluble acid melting at 161° distills under reduced pressure (20 mm.) almost without decomposition, but, when slowly heated under ordinary pressures, it is gradually converted into the lactone of the acid of melting point 132° . The *cis*- and *trans*-hydroxy-acids react readily with hydrobromic acid with formation of the corresponding *cis*- and *trans*-2-bromo-1-methylcyclohexane-4-carboxylic acids,



which are isomeric with the 1-bromo-acid previously prepared (p. 1417) and, like this acid, both yield 1-methyl- Δ^1 -cyclohexene-4-carboxylic acid,



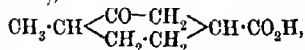
by elimination of hydrogen bromide.

It was thought probable that one of the modifications of the bromo-acid might lose hydrogen bromide with formation of the Δ^2 -acid, but there was no evidence of this and the elimination apparently takes place entirely in the direction of the methyl group.

We have now been able to work out a method, based on the above facts, for the preparation of 1-methyl- Δ^1 -cyclohexene-4-carboxylic acid which is less laborious than that described at the beginning of this paper, and this method is described on p. 1425.

During the course of this investigation we studied the action of oxidising agents on the *cis*- and *trans*-modifications of 1-methylcyclohexan-2-ol-4-carboxylic acid and obtained interesting results which may be briefly summarised as follows.

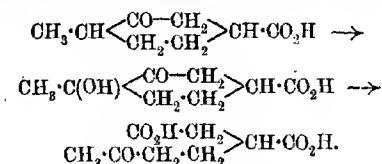
The *cis*-acid is rather readily attacked by chromic acid mixture with formation of 1-methylcyclohexan-2-one-4-carboxylic acid (γ -keto-hexahydro-*p*-toluic acid),



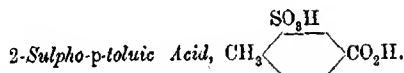
which melts at $112-113^\circ$ and yields a sparingly soluble semicarbazone (m. p. 152°) and a sparingly soluble oxime (m. p. 186°). When this

acid is oxidised by chromic acid, it is converted into a new keto-dibasic acid, $C_8H_{12}O_6$, which melts at 120° and yields a *semicarbazone* which decomposes at 183° and a readily soluble *oxime* (m. p. about 140°).

There can be no doubt that this acid is β -carboxy- δ -acetylvaleric acid, $CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CH(CO_2H) \cdot CH_2 \cdot CO_2H$, and its formation is readily explained by the following scheme:



The *trans*-hydroxy-acid is attacked by chromic acid with much more difficulty than the *cis*-modification, and we were unable to isolate 1-methylcyclohexan-2-one-4-carboxylic acid as a product of oxidation. Under the conditions which had to be employed, this latter acid evidently undergoes further oxidation, since the product consisted entirely of β -carboxy- δ -acetylvaleric acid.



The sulphonation of *p*-toluic acid appears to have been first carried out by Fischli (*Ber.*, 1879, 12, 616), who prepared 2-sulpho-*p*-toluic acid in this way and examined several of its salts.

Subsequently Weinreich (*Ber.*, 1887, 20, 982) investigated this sulphonic acid and showed that, when fused with potassium hydroxide, it is converted into 2-hydroxy-*p*-toluic acid. In preparing large quantities of 2-sulpho-*p*-toluic acid we have found that the following process yields excellent results.

p-Toluic acid (200 grams) is heated with fuming sulphuric acid (monohydrate, 500 c.c.) in a strong flask on the sand-bath, the temperature being kept at 150° by a regulator placed in the mixture. The *p*-toluic acid dissolves in the sulphuric acid and is readily sulphonated, and, after eight hours, the cold product is mixed with water (650 c.c.), when the sulphonic acid crystallises at once. In order to obtain it in a better condition for filtering, the whole is heated until solution is complete and then allowed to cool slowly. The mass of crystals is then collected on glass wool or flannel by the aid of the pump, dissolved in hot water (600 c.c.), the solution filtered, concentrated, and allowed to crystallise, when the pure sulphonic acid is obtained in a yield of about 380 grams. Meyer and Baur

(*Annalen*, 1883, 220, 19) state that this sulphonic acid has the composition $C_8H_7O_2SO_3H \cdot 2H_2O$, and that, when exposed over sulphuric acid in a vacuum desiccator, it loses water and becomes $C_8H_7O_2SO_3H \cdot H_2O$, but our analytical results do not confirm this statement. We crystallised two different specimens of the sulphonic acid from glacial acetic acid and, after allowing the crystals to remain in the air until free from acetic acid, the composition was determined by titration with standard sodium hydroxide.

I. 0.224 neutralised 0.077 NaOH. Equivalent = 116.1.

II. 0.628 " 0.2147 NaOH. " = 116.8.

The equivalent of $C_8H_7O_2SO_3H \cdot H_2O$ is 117.

Some of the acid was then crystallised from water, from which it separated in slender, colourless needles which, after drying in the air at the ordinary temperature, gave the following results on titration:

I. 0.5426 neutralised 0.1596 NaOH. Equivalent = 135.9.

II. 0.3016 " 0.0895 NaOH. " = 134.7.

The equivalent of $C_8H_7O_2SO_3H \cdot 3H_2O$ is 135.

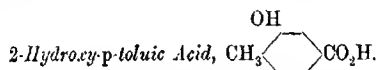
It appears therefore that the sulphonic acid crystallises from water with $3H_2O$ and from acetic acid with $1H_2O$.

The *barium hydrogen* salt, $(C_8H_7O_2S)_2Ba \cdot 5H_2O$.—This characteristic salt is readily obtained when the solution of the sulphonic acid (5 grams) in water is digested with barium carbonate, filtered, and the hot filtrate mixed with 5 grams of the sulphonic acid. On cooling, the sparingly soluble salt separates in brilliant flat plates.

0.8972 gave 0.3190 $BaSO_4$. $Ba = 20.9$.

0.6918 neutralised 0.0842 NaOH. Equivalent = 328.3.

$(C_8H_7O_2S)_2Ba \cdot 5H_2O$ requires $Ba = 20.82$ per cent. and equivalent = 328.5.



Weinreich (*Ber.*, 1887, 20, 982) prepared this acid from 2-sulpho-*p*-toluic acid by fusion with four times its weight of potassium hydroxide, but he gives no details of temperature and time of fusion.

In preparing large quantities of the hydroxy-acid, we have found the following process to give excellent results. Potassium hydroxide (1 kilo.) is moistened with very little water and heated in a large nickel crucible at 200° ; the sulphonic acid (356 grams) is then added in small quantities at a time, and the temperature gradually raised to 260° and maintained at this point until the fusion is perfectly fluid. The almost colourless product is dissolved in water, neutralised with sulphuric acid, the potassium sulphate removed by filtration, and the

filtrate acidified with hydrochloric acid, when the hydroxy-acid separates at once in a crystalline condition.

The mass is collected, washed, and recrystallised from water, from which it separates in colourless needles, melting at 206—207°, the yield being 187 grams. Weinreich (*loc. cit.*) states that this acid is volatile in steam, but we found that it was carried over only with great difficulty; he also obtained terephthalic acid as one of the products of the fusion, but none of this acid was formed during our experiments. Probably Weinreich's sulphonic acid contained some unchanged *p*-toluic acid, which would doubtless yield terephthalic acid on fusion with potassium hydroxide.

Reduction of 2-Hydroxy-p-toluic Acid.

The conversion of 2-hydroxy-*p*-toluic acid into the *cis*- and *trans*-modifications of 1-methylcyclohexan-2-ol-4-carboxylic acid by reduction with sodium and alcohol was carried out under the following conditions. The hydroxy-acid (40 grams) was dissolved in alcohol (1250 c.c.) in a large flask fitted with a long and efficient condenser, the solution heated to boiling, and then sodium (150 grams) added as quickly as possible. As soon as the sodium had dissolved, the product was mixed with water (300 c.c.), the solution nearly neutralised with hydrochloric acid, evaporated to a small hulk, acidified, and extracted many times with ether. The ethereal solution was dried, evaporated, and the residue, which on standing becomes semi-solid, was esterified by leaving it in contact with four times its weight of 4 per cent. alcoholic hydrogen chloride for forty-eight hours.*

The product was dissolved in ether, washed with water and dilute sodium carbonate, dried, and fractionated several times under reduced pressure, when a large fraction 157—163° (20 mm.) was obtained, which consisted of the esters of the mixed *cis*- and *trans*-acids. In order to hydrolyse this ester, it (90 grams) was dissolved in methyl alcohol (200 c.c.) and potassium hydroxide (45 grams) in the cold, and, after remaining for twenty-four hours, the crystals (27 grams), which had separated, were collected and washed with a little methyl alcohol. The colourless salt was dissolved in water, evaporated until free from methyl alcohol, and acidified, when a solid acid separated, which crystallised from water in short prisms, melted at 130—132°, and consisted of pure *cis*-1-methylcyclohexan-2-ol-4-carboxylic acid. The filtrate from the potassium salt was mixed with water, nearly neutral-

* An alternative method is to leave the semi-solid mass in contact with porous porcelain until free from oil and then to crystallise the residue fractionally from ether and then from water. The porous plates are extracted with ether and the crude syrupy acid purified by conversion into the ester, &c.

ised with hydrochloric acid, evaporated until free from methyl alcohol, acidified, and, after remaining for twenty-four hours, the crystalline acid was collected, drained on porous porcelain, and crystallised from ether, from which the pure *trans*-acid separated in rectangular plates melting at 160—161°. The mother liquors yield, on extraction with ether, a mixture of the *cis*- and *trans*-acids, which may be separated by repeated crystallisation, first from ether and then from water, or better by converting into the ester, fractionating this, and then hydrolysing with potassium hydroxide in the way described above. As far as could be determined from rough weighings, the *cis*- and *trans*-acids are produced in the above process in the proportion, approximately, of 3:2.

Cis-1-Methylcyclohexan-2-ol-4-carboxylic Acid.

The preparation of this acid is described in the preceding section. It is much more soluble both in ether and in water than the corresponding *trans*-acid, and separates from water in small, glistening prisms melting at 130—132°:

0.1546 gave 0.3430 CO_2 and 0.1216 H_2O . C = 60.5; H = 8.7.

0.1551 " 0.3456 CO_2 " 0.1233 H_2O . C = 60.7; H = 8.8.

$\text{C}_8\text{H}_{14}\text{O}_3$ requires C = 60.8; H = 8.8 per cent.

The Lactone.—In preparing this substance, the crude *cis*-acid was slowly distilled under 20 mm. pressure, when much water was eliminated and, after this had passed over, a quantity of a viscid syrup distilled at about 125—170°, leaving a considerable residue.

The distillate was twice fractionated, and yielded a quantity of a colorless oil, which distilled constantly at 128—130°/17mm., and solidified completely when it was left for twenty-four hours in the ice chest.

The crystals were freed from oil by contact with porous porcelain, and washed with a little light petroleum, in which the lactone is sparingly soluble:

0.1190 gave 0.2985 CO_2 and 0.0940 H_2O . C = 68.4; H = 8.8.

$\text{C}_8\text{H}_{12}\text{O}_2$ requires C = 68.6; H = 8.6 per cent.

This lactone melts at 30—33° and, especially when warm, has a pronounced odour of camphor. It dissolves in hot water, yielding an acid solution, but hydrolysis takes place only very gradually, since, even after boiling for several minutes, the addition of ammonium sulphate causes most of the lactone to separate. It was hydrolysed by boiling with sodium carbonate, and the solution acidified and extracted with ether. The ethereal solution was dried and evaporated, when a crystalline residue was obtained, which, after crystallisation from water, melted at 130—132°, and consisted of the pure *cis*-acid.

cis-2-Bromo-1-methylcyclohexane-4-carboxylic Acid and its Conversion
into 1-Methyl- Δ^1 -cyclohexene-4-carboxylic Acid.

The *cis*-hydroxy-acid dissolves readily in fuming aqueous hydrobromic acid (saturated at 0°), but the formation of the bromo-acid does not appear to take place until the solution is heated on the water-bath, when it clouds and separates into two layers. On standing in the ice-chest, the upper layer gradually solidifies to a gelatinous solid, which is washed well, left in contact with porous porcelain until quite dry, and then crystallised from light petroleum (b. p. 60—70°):

0.2508 gave 0.2129 AgBr. Br = 36.1.

$C_8H_{15}O_2Br$ requires Br = 36.2 per cent.

This *cis*-bromo-acid becomes red at 105°, melts and decomposes at about 118°, and is very readily soluble in formic acid, chloroform, alcohol, or benzene. It separates, when its concentrated solution in formic acid is cooled in ice, in thin glistening plates.

When warmed with water it dissolves completely, but decomposition, with elimination of hydrogen bromide, takes place only gradually, even when the solution is boiled.

The *cis*-bromo-acid is readily decomposed by boiling with five times its weight of anhydrous pyridine, and, if the bulk of the pyridine is removed by evaporation on the water-bath and the residue mixed with hydrochloric acid, a solid acid separates which, after crystallisation from light petroleum, melts at 97—99°:

0.1817 gave 0.4559 CO_2 and 0.1421 H_2O . C = 68.5; H = 8.7.

$C_8H_{12}O_2$ requires C = 68.6; H = 8.6 per cent.

That this acid is 1-methyl- Δ^1 -cyclohexene-4-carboxylic acid was proved by mixing it with a specimen which had been prepared from δ -keto-hexahydrobenzoic acid (Trans., 1904, 85, 664), when the mixture melted at 98—99°.

trans-1-Methylcyclohexan-2-ol-4-carboxylic Acid.

When quite pure, this acid is sparingly soluble in ether or cold water, and separates from these solvents in glistening rectangular plates melting at 160—161°:

0.1466 gave 0.3276 CO_2 and 0.1152 H_2O . C = 60.8; H = 8.7.

0.1617 „ 0.3608 CO_2 „ 0.1287 H_2O . C = 60.8; H = 8.8.

$C_8H_{14}O_3$ requires C = 60.8; H = 8.8 per cent.

When this *trans*-hydroxy-acid is heated under 15 mm. pressure, it distills apparently without decomposition, but if distillation is conducted under the ordinary pressure, water is eliminated and an oil passes over at about 260°. The distillate was dissolved in ether, dried,

and twice refractionated, when a considerable quantity of oil distilled at about $138^{\circ}/25$ mm. and crystallised on cooling. After draining on porous porcelain the crystals melted at 28° – 30° , and consisted of the lactone of the *cis*-hydroxy-acid, since they yielded the *cis*-acid, melting at 129 – 132° , on hydrolysis. It is therefore possible in this way to convert the *trans*-hydroxy-acid into the corresponding *cis*-modification.

trans-2-Bromo-1-methylcyclohexane-4-carboxylic Acid and its Conversion into 1-Methyl- Δ^1 -cyclohexene-4-carboxylic Acid.

The *trans*-hydroxy-acid dissolves readily in fuming hydrobromic acid (saturated at 0°) and the solution remains clear for several hours, but when heated on the water-bath, separation into two layers readily takes place. The product, which showed no signs of crystallising, was mixed with water, extracted with ether, the ethereal solution dried and evaporated, and the viscid syrupy residue converted into the ester by dissolving in 10 per cent. alcoholic sulphuric acid in the cold. After twenty-four hours, the ester was precipitated by water, extracted with ether, the ethereal solution washed with dilute sodium carbonate, dried, evaporated, and distilled, when the crude bromo-ester passed over at about 170 – $175^{\circ}/100$ mm., but yielded, on analysis, only 19.6 instead of 32.2 per cent. of bromine. This low percentage of bromine is doubtless due to the presence of unsaturated ester, produced by the elimination of hydrogen bromide during the preparation and purification of the bromo-ester. The oil was now digested with diethylaniline (5 vols.) for one hour, the product dissolved in ether, washed thoroughly with dilute hydrochloric acid, and then with sodium carbonate, dried, and evaporated. The residual oil distilled almost constantly at about $148^{\circ}/100$ mm., and consisted of ethyl 1-methyl- Δ^1 -cyclohexene-4-carboxylate:

0.1221 gave 0.3181 CO_2 and 0.1045 H_2O . $\text{C} = 70.9$; $\text{H} = 9.5$.

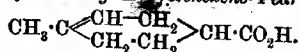
$\text{C}_{10}\text{H}_{16}\text{O}_2$ requires $\text{C} = 71.4$; $\text{H} = 9.5$ per cent.

This ester was hydrolysed by leaving it in contact with alcoholic potash for twenty-four hours, water was then added, the solution saturated with carbon dioxide, evaporated until free from alcohol, and acidified, when a solid mass separated, which was collected and crystallised from dilute acetic acid:

0.1211 gave 0.3036 CO_2 and 0.0944 H_2O . $\text{C} = 68.4$; $\text{H} = 8.6$.

$\text{C}_8\text{H}_{12}\text{O}_2$ requires $\text{C} = 68.6$; $\text{H} = 8.6$ per cent.

This acid melted at 98 – 99° , and was 1-methyl- Δ^1 -cyclohexene-4-carboxylic acid, since, when mixed with a specimen which had been prepared on a previous occasion (Trans., 1904, 85, 664), there was no change in the melting point.

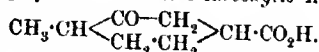
Preparation of 1-Methyl-Δ¹-cyclohexene-4-carboxylic Acid,

The crude mixture of the esters of the *cis*- and *trans*-modifications of 1-methylcyclohexan-2-ol-4-carboxylic acid, obtained as described on p. 1421, is fractionated under 20 mm. pressure, and the fraction 150—170° hydrolysed by methyl-alcoholic potash. The syrupy hydroxy-acid is dissolved in five times its weight of fuming hydrobromic acid (saturated at 0°), and, after remaining overnight, the solution is heated for half an hour on a rapidly-boiling water-bath; the dark brown product is then poured into water and extracted with ether.

After drying and evaporating, the crude bromo-acid is dissolved in five times its volume of 10 per cent. alcoholic sulphuric acid, and left for two days. The ester is precipitated by water, extracted by ether in the usual way, and distilled under 20 mm. pressure, in order to separate it from a considerable quantity of resinous matter which is always produced.

The almost colourless distillate is boiled with four times its volume of diethylaniline, the product dissolved in ether, repeatedly extracted with a large excess of dilute hydrochloric acid, dried, evaporated, and fractionated, when almost the whole quantity passes over at 147—148°/100 mm., and consists of nearly pure ethyl 1-methyl-Δ¹-cyclohexene-4-carboxylate.

When this ester is left in contact with half its weight of potash dissolved in methyl alcohol, hydrolysis rapidly takes place, and, after twelve hours the product is nearly neutralised with hydrochloric acid, evaporated until free from alcohol, cooled, and acidified, and the solid acid collected and washed with water. If the acid is now dissolved in a slight excess of dilute sodium carbonate, digested for a few minutes on the water-bath with purified animal charcoal, filtered, and reprecipitated, it is obtained perfectly colourless and pure enough for most purposes. In this condition it usually melts at 94—97°, but on crystallisation from light petroleum or dilute acetic acid at once raises the melting point to 98—99°. The yield of 1-methyl-Δ¹-cyclohexene-4-carboxylic acid, obtained from 250 grams of *p*-toluic acid, is frequently as much as 70 grams.

1-Methylcyclohexan-2-one-4-carboxylic Acid,

This acid was prepared by the oxidation of *cis*-1-methylcyclohexan-2-ol-4-carboxylic acid under the following conditions :

The crude *cis*-acid (30 grams) was dissolved in water (150 c.c.), and oxidised by the gradual addition of potassium dichromate (40 grams) and sulphuric acid (30 c.c.) in water (150 c.c.), the temperature being kept at 75° during the operation. The product was saturated with ammonium sulphate, extracted with ether in a continuous extraction apparatus, the ethereal solution dried, evaporated, and the crude, syrupy residue (25 grams) esterified by leaving it in contact with 2.5 per cent. alcoholic hydrogen chloride (100 c.c.) for four days. After diluting with water, the ester was extracted with ether, the ethereal solution well washed with dilute sodium carbonate, dried, evaporated, and the oily residue repeatedly fractionated, when about 10 grams of oil were obtained, which distilled constantly at 146–148°/25 mm., possessed a rather pleasant fruity odour, and consisted of almost pure *ethyl 1-methylcyclohexan-2-one-4-carboxylate*:

0.1801 gave 0.4268 CO₂ and 0.1439 H₂O. C = 64.6; H = 8.8.

C₁₀H₁₆O₃ requires C = 65.2; H = 8.7 per cent.

This ester was digested with hydrochloric acid (10 c.c.) and water (60 c.c.) for four hours, the clear solution evaporated until free from alcohol, saturated with ammonium sulphate, and repeatedly extracted with ether. The ethereal solution was then dried and evaporated, when a colourless syrup was obtained, which gradually crystallised, and, after remaining in contact with porous porcelain until quite free from oil, the keto-acid was further purified by crystallisation from ether:

0.1520 gave 0.3430 CO₂ and 0.1030 H₂O. C = 61.5; H = 7.5.

C₈H₁₂O₃ requires C = 61.5; H = 7.7 per cent.

1-Methylcyclohexan-2-one-4-carboxylic acid melts at 112–113° with slight previous softening, and is readily soluble in water. It is sparingly soluble in cold ether, but dissolves rather readily in the boiling solvent, and separates from the concentrated solution in hard crusts.

The *oxime* was prepared by adding hydroxylamine hydrochloride and excess of potassium hydroxide to a saturated aqueous solution of the acid. After remaining for twenty-four hours, the product was acidified, and the crystalline oxime which separated extracted with large quantities of ether. The ethereal solution was dried, and concentrated until crystals began to separate from the boiling solution:

0.1777 gave 13.4 c.c. N₂ at 21° and 758 mm. N = 8.5.

C₈H₁₃O₃N requires N = 8.2 per cent.

When crystallised from ether, this oxime melts at about 186° and is characterised by being very sparingly soluble in ether; it dissolves readily in boiling water, and separates from the concentrated solution in short prisms grouped together like cactus leaves and melting at about 193–195°.

The *semicarbazone* separates immediately, as a granular precipitate,

OF 1-METHYLCYCLOHEXAN-2-OL-4-CARBOXYLIC ACID. 1427

when the aqueous solution of the keto-acid is mixed with a strong solution of semicarbazide hydrochloride and sodium acetate.

It was collected, washed with water, followed by alcohol, and dried at 100°:

0.1060 gave 18.5 c.c. N_2 at 21° and 756 mm. $N = 19.7$.

$C_9H_{15}O_3N$ requires $N = 19.7$ per cent.

When purified in this way this semicarbazone melted at about 193—195° with slow decomposition. It is very sparingly soluble in water or alcohol, and separates from much boiling water as a glistening, microcrystalline powder.

β-Carboxy-δ-acetylvaleric Acid,
 $CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CH(CO_2H) \cdot CH_2 \cdot CO_2H$.

It has been pointed out in the introduction (p. 1419) that, whilst *cis*-1-methylcyclohexan-2-ol-4-carboxylic acid is converted into 1-methylcyclohexan-2-one-4-carboxylic acid by oxidation with chromic acid mixture, the corresponding *trans*-acid is attacked by the oxidising agent with much greater difficulty, and then with formation of *β*-carboxy-δ-acetylvaleric acid. The pure *trans*-acid (6 grams) was dissolved in the least possible quantity of hot water, and oxidised on the water-bath by the gradual addition of potassium dichromate (9 grams) and sulphuric acid (8 c.c.) dissolved in water (50 c.c.).

As soon as oxidation was complete, the green solution was saturated with ammonium sulphate, extracted 10 times with ether, the ethereal solution dried and evaporated, when a syrup was obtained which gradually crystallised. After remaining in contact with porous porcelain until free from traces of oil, the colourless mass was crystallised from ether;

0.1492 gave 0.2800 CO_2 and 0.0890 H_2O . $C = 51.1$; $H = 6.6$.

$C_8H_{12}O_5$ requires $C = 51.1$; $H = 6.4$ per cent.

The basicity of the acid was determined by titration with decinormal sodium hydroxide, when 0.1510 required 0.0644 NaOH for neutralisation, whereas this amount of a dibasic acid, $C_8H_{12}O_5$, should neutralise 0.0643 NaOH.

β-Carboxy-δ-acetylvaleric acid melts at 119—120°, is readily soluble in water, but sparingly so in ether, and separates in brilliant crystals when the solution, in much ether, is concentrated.

The presence of the $CH_3 \cdot CO$ group in the acid is indicated by the fact that it is readily attacked by potassium hypobromite with immediate separation of bromoform.

The *oxime* was prepared by mixing a strong solution of the potassium salt of the acid with hydroxylamine hydrochloride and potassium hydroxide; after twelve hours, the product was acidified

and repeatedly extracted with ether. The ethereal solution was dried and evaporated, when a readily soluble, colourless syrup was obtained which gradually crystallised and in fourteen days had become quite hard. The mass was ground with light petroleum, transferred to porous porcelain, and, when quite free from oil, dissolved in acetone, the solution mixed with benzene and the acetone evaporated. After some time, the benzene solution deposited the oxime as a hard crystalline crust:

0.1350 gave 7.9 c.c. N_2 at 23° and 770 mm. $N = 6.7$.

$C_8H_{13}O_2N$ requires $N = 6.9$ per cent.

This oxime has no definite melting point; it softens at 130° and melts gradually between 135° and 140° , becoming orange red and evolving gas. It is readily soluble in alcohol, ether, or acetone, but sparingly so in benzene or light petroleum.

The semicarbazone.—A concentrated solution of the acid gives no immediate precipitate with semicarbazide hydrochloride and sodium acetate, but when the solution is warmed and the containing vessel rubbed with a glass rod, the semicarbazone soon separates as a colourless granular precipitate, which is collected, washed with water, and dried at 100° . On analysis:

0.1055 gave 15 c.c. N_2 at 18° and 760 mm. $N = 16.3$.

$C_9H_{15}O_3N_2$ requires $N = 17.1$ per cent.

When *cis*-1-methylcyclohexan-2-one-4-carboxylic acid is oxidised under the conditions observed in the case of the *trans*-acid, it yields a syrup which gradually crystallises. This was converted into the semicarbazone and the keto-acid regenerated by treatment with dilute hydrochloric acid and extraction with ether, when a colourless solid was obtained which, after crystallisation from ether, melted at 119 – 120° , and consisted of β -carboxy- δ -acetylvaleric acid:

0.1206 gave $0.2244 CO_2$ and $0.0700 H_2O$. $C = 50.8$; $H = 6.4$.

$C_8H_{12}O_5$ requires $C = 51.1$; $H = 6.4$ per cent.

Since it is shown on p. 1425 that the first product of the oxidation of the *cis*-acid is 1-methylcyclohexan-2-one-4-carboxylic acid, it follows that β -carboxy- δ -acetylvaleric acid is produced from this keto-acid by the further action of the oxidising agent.

The authors wish to thank Mr. W. N. Haworth for valuable assistance, and especially for carrying out most of the analyses contained in this communication. They also wish to state that part of the expense of this investigation was defrayed by a grant from the Executive Committee of the Carnegie Trust.

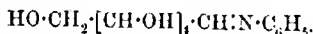
THE UNIVERSITY,
MANCHESTER.

CXXXVIII.—*The Constitution of Glucose Derivatives.*
Part I. Glucose-anilide, -oxime, and -hydrazone.

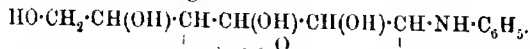
By JAMES COLQUHOUN IRVINE, Ph.D., D.Sc., and ROBERT GILMOUR.

THE use of an aldehydic formula for glucose and other reducing aldoses has been largely discontinued since the discovery of the isomeric alkyl glucosides, and the study of the isodynamic changes undergone by sugars in solution has strengthened the arguments which support the alternative γ -oxidic formulae. Although there seems no reasonable doubt that the reducing sugars in solution, or in their condensation reactions with hydroxy-compounds, behave as γ -oxides, yet many reactions remain, such as the formation of anilides, oximes, or hydrazones, which seem capable of simpler explanation on the assumption that the sugar is merely participating in a typical aldehydic reaction.

Throughout the literature occasional references are, however, found which show that the possibility of applying a γ -oxidic formula even to compounds usually regarded as aldehydic derivatives has not escaped notice, the reactions of some sugar derivatives being somewhat divergent from those which might be expected from compounds possessing a straight-chain structure. Thus, the constitution of glucoseanilide has been debated ever since the discovery of the compound. According to the original simple formula proposed by Schiff and supported by Strauss (*Ber.*, 1894, 27, 1287), the substance possesses the structure



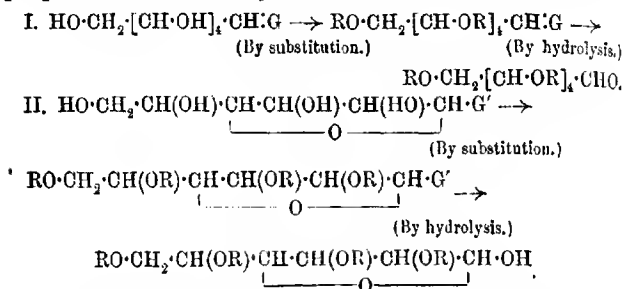
On the other hand, Sorokin and Marchlewski (*J. pr. Chem.*, 1894, [ii], 50, 95) maintain that the condensation of the sugar and the base is not an aldehydic reaction, and that the product possesses the γ -linking characteristic of glucosides:



In the particular case of glucoseanilide, it may be maintained that the details of the constitutional structure are not of special importance, but the fact that even in the case of such a simple compound two alternative formulae have been proposed, raises the question as to whether other condensation products of sugars and nitrogen bases might also be referred to the γ -oxidic form of the sugar. This would involve a revision of the constitutional formulae of many substances, such as oximes and hydrazones, which have played an important part in the development of the chemistry of the sugars, and also of such

compounds as glucosamine, glucosimine, glucosureide, &c., which are of special interest on account of their probable relationship to the gluco-proteins.

Evidence regarding the internal linking of a sugar condensation product must be sought for in the preparation of derivatives and examination of the substituted sugar formed on hydrolysis. Thus, if in the two types of condensation derivatives theoretically obtainable from glucose we substitute the hydroxyl groups by the groups OR, then, on hydrolysis, either a penta- or a tetra-substituted glucose will be formed according as to whether the original compound was derived from a hydroxy-aldehyde or a γ -oxide. These alternatives are expressed in the following scheme, in which G or G' represents the group condensed with the sugar residue :



Acetyl or benzoyl derivatives are not adapted for such work, as the substituting groups are lost during hydrolysis, and the parent sugar is thus regenerated, but alkylated derivatives, which retain the etheric groups on hydrolysis, are suitable compounds on which to study the above reactions.

These considerations have already been applied in papers published from this laboratory, in which the structural linking of the glucose residue in sucrose, maltose, methyl glucoside, and salicin (Trans., 1903, 83, 1028; 1905, 87, 1025; 1906, 89, 814) has been subjected to experimental proof, and in a recent publication (Trans., 1908, 93, 94) the method has been applied to elucidating the structural formulae of the oxime and anilide obtained from tetramethyl glucose. All the compounds mentioned were recognised as γ -oxides, as, after complete alkylation and hydrolysis of the products thus obtained, tetramethyl glucose was produced in each case. As this sugar is capable of forming a definite lactone, this result shows that each of the parent substances must have contained the linking $\begin{smallmatrix} \text{C}\cdot\text{C}\cdot\text{C}\cdot\text{C} \\ \text{---O---} \end{smallmatrix}$. The last-mentioned research on tetramethyl glucoseanilide and tetramethyl glucoseoxime was undertaken in the hope of preparing by alkyl-

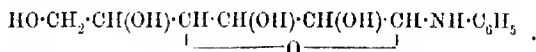
ation and subsequent hydrolysis the aldehydic form of pentamethyl glucose, and the above result was therefore unexpected. As, however, a very close parallel exists between alkylated sugars and the parent aldoses, it suggested that the constitution of glucose-oxime and anilide should be further examined. Our results have shown the necessity of extending the scope of the work so as to include the study of more examples of sugar derivatives; in the meantime, we submit our deductions as to the structure of glucose-oxime, -anilide, and -hydrazone.

We find that glucoseanilide is formed, not only by heating glucose and aniline in alcoholic solution, but that condensation takes place slowly when an ethyl-alcoholic solution of glucose is mixed with an excess of aniline and kept in the cold. A polarimetric examination of the process was thus possible. It was found that the initial dextrorotation of the solution at first increased steadily throughout five days and then diminished gradually, finally becoming constant when a decided levorotation was recorded. This rise and subsequent fall in the rotatory power resembles the converse optical changes which accompany the conversion of glucose into a mixture of α - and β -methyl-glucosides, and points at once to the fact that two forms of glucoseanilide exist. The first of these isomerides to be formed must possess a greater dextrorotation than that of glucose, and this labile form is gradually converted into the more stable levorotatory variety.

Towards the end of the condensation, the anilide commenced to crystallise out from the solution. The first crop to separate was dextrorotatory ($[\alpha]_D + 10.7^\circ$), and, contrary to expectation, displayed mutarotation in methyl-alcoholic solution, the permanent value recorded being $[\alpha]_D - 52.4^\circ$. Apparently mutarotation has not hitherto been observed in the case of glucoseanilide, the optical rotatory power of a 3 per cent. solution in methyl alcohol being quoted as a permanent value ($[\alpha]_D - 49.1^\circ$). This failure to observe the phenomenon is, however, readily explained, as we find that the change is extremely rapid, particularly in the presence of traces of hydrogen chloride. The study of the mutarotation, given in detail in the experimental part, indicates that two stereoisomeric modifications of the anilide exist, one dextro- and the other levo-rotatory, and that the solution of permanent rotatory power contains a large excess of the latter form. The fact that glucoseanilide exists in two forms which are interconvertible is, of course, no proof in itself that the substance possesses the glucosidic structure, but the results bring the compound into line with mutarotatory sugars and with the glucosides which have been shown to display similar optical changes in cases where their interconversion has been studied. Direct experimental evidence was, however, obtained by applying the silver

oxide method of methylation to glucoseanilide. This reaction, owing to the instability of the compound, involved greater difficulty than any of the methylations we have previously attempted in the sugar group. As the alkylation proceeded, however, the partly methylated product resisted the oxidising effect of the silver oxide, and the final treatment with the latter was carried out as usual in methyl iodide solution. An oil was finally obtained which crystallised completely. After recrystallisation from methyl alcohol, the product was recognised as tetramethyl glucoseanilide, identical with that produced directly from tetramethyl glucose. The analytical composition and melting point (132—134°) agreed closely, and the specific rotation of a 3 per cent. solution in acetone was $[\alpha]_D +236.4^\circ$, the value previously found for a specimen prepared directly from tetramethyl glucose being $[\alpha]_D +229.5^\circ$. This discrepancy in the optical values may be readily explained, as we find that the specimen of tetramethyl glucoseanilide previously prepared from tetramethyl glucose, when further recrystallised from methyl alcohol instead of from ether, shows the maximum specific rotation $[\alpha]_D +238.4^\circ$ in acetone solution. This result at once establishes the constitution of glucoseanilide. The compound must have the same general structure as tetramethyl glucoseanilide, and it has already been shown (*loc. cit.*) that the latter contains the γ -oxidic linking. The proof was extended by hydrolysing the alkylated anilide obtained from glucoseanilide as explained above; as was expected, the characteristic tetramethyl glucose was isolated from the reaction.

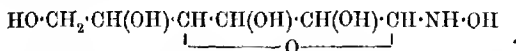
Assuming, as from past experience we are justified in doing, that the alkylating mixture of silver oxide and methyl iodide exercises no disturbing effect on the molecular arrangement, the only formula for glucoseanilide which will satisfactorily account for these reactions is



Such a compound could exist in two modifications (α and β), the interconversion of which would account for the mutarotation.

We have also obtained results showing that glucoseoxime possesses a structure similar to that of tetramethyl glucoseoxime, and does not therefore react in every case as a normal oxime. The compound was methylated by the joint action of silver oxide and methyl iodide, first in aqueous methyl-alcoholic solution, then in pure methyl alcohol, and finally, when the alkylation had proceeded far enough, in methyl iodide solution. The product, after five successive alkylations, was fractionated under diminished pressure, then re-alkylated, and finally purified by vacuum distillation. A colourless syrup was thus obtained, which was proved by analysis to be tetramethyl glucoseoximo methyl ether,

from which, moreover, tetramethyl glucose was produced by hydrolysis. It seems hardly possible that the methylation could have been incomplete after the prolonged and repeated alkylation to which the compound had been subjected, and thus we conclude that only five methyl groups can enter the molecule of glucoseoxime. Of the methoxyl groups thus formed, one must be united to nitrogen as it is removed on hydrolysis. The four remaining groups are therefore attached to the sugar residue in the same manner as in tetramethyl glucose. These considerations point to the following formula for glucoseoxime :



It must be admitted that, although the above formula accounts for the existence of the oxime in two, presumably inconvertible, stereoisomeric forms, it does not readily explain many of the reactions of the compound. Thus a hexa-acetate has been obtained from glucose *anti*-aldoxime, whilst the *syn*-form is reduced to glucamine, and yields on acetylation penta-acetylglucononitrile. The reagents necessary for these changes are, however, presumably more liable to cause molecular rearrangement than the neutral alkylating mixture we have used, and, although Wohl's work shows that the compound behaves as a normal oxime towards powerful reagents, our results indicate that the compound is equally capable of reacting as a γ -oxide towards neutral reagents.

The application of the alkylation process to glucosephenylhydrazine was entirely unsuccessful. The attempted methylation was carried out first in methyl-alcoholic solution, and afterwards in methyl iodide solution, the details of the process being the same as already described for glucoseanilide. After each treatment with the alkylating mixture, the solubility of the product in organic solvents increased as usual, but the nitrogen content diminished steadily. The only product isolated was a syrupy liquid (b. p. 134—138° under 15 mm. pressure), which contained no nitrogen and which in appearance and behaviour towards Fehling's solution resembled an alkylated glucoside. The syrup when redistilled gave a lower boiling portion, showing $[\alpha]_D^{20} - 2.2^\circ$ in methyl alcohol; the higher boiling fraction, on the other hand, was slightly dextrorotatory ($[\alpha]_D^{20} + 11.0^\circ$).

These liquid products gave, on analysis, figures agreeing approximately with those required for a fully methylated methyl glucoside, but, nevertheless, they did not consist of mixtures of α - and β -tetramethyl methyl glucosides, as, on hydrolysis, the specific rotation only increased to the value $[\alpha]_D + 12.2^\circ$, and the reducing sugar thus formed not only failed to crystallise, but showed a very small dextro-

rotation in aqueous solution. These, results, for which we are unable to offer a satisfactory explanation, bear a marked resemblance to those obtained by Irvine and Cameron (Trans., 1905, 87, 907) in the alkylation of syrupy methyl galactoside.

Apparently the reaction between silver oxide, methyl iodide, and glucosephenylhydrazone is extremely complex, and does not consist in the first place of simple molecular rupture. In such a case, the glucose thus liberated would be converted into dimethyl oxalate, which is the final product formed in the reaction between silver oxide, methyl iodide, and glucose. In all probability the silver oxide exerts a vigorous oxidising action on the compound, but, in addition, we find that methyl iodide readily decomposes a methyl-alcoholic solution of the hydrazone at 100° with the formation of dark-coloured resinous compounds.

The failure to alkylate glucosephenylhydrazone was not unexpected, as previous attempts to methylate tetramethyl glucosephenylhydrazone led to no positive result.

EXPERIMENTAL.

Preparation and Alkylation of Glucoseanilide.

The glucoseanilide required was prepared partly by Sorokin's method (Ber., 1886, 19, 513) and also by mixing an alcoholic solution of glucose (1 mol.) with a large excess (5 mols.) of aniline and preserving the solution for three weeks at about +6°. In the latter case, the compound was deposited in successive crops, which were purified by dissolving in methyl alcohol, precipitating with ether, and drying in a vacuum.

Preliminary alkylation experiments showed that the addition of silver oxide to a solution of the substance in methyl alcohol containing methyl iodide resulted in vigorous oxidation. The product was strongly acid and very dark in colour, and analysis of the silver residues showed that 25 per cent. of the silver oxide had been reduced to the metallic state. The process was therefore modified so as to maintain the temperature of the reaction as low as possible during the early stages of the alkylation.

Twenty grams of the anilide (1 mol.) were dissolved in 50 c.c. of methyl alcohol, and a mixture containing 100 grams of methyl iodide (10 mols.) and 50 c.c. of ether added to the cold solution. This was placed in a wide-mouthed bottle connected with an inverted condenser and provided with a stirring apparatus working in a mercury joint, the bottle being surrounded by a cooling jacket through which water at 10° was circulated. The finely-powdered silver oxide (5 mols.) was added in small quantities, the additions extending over six hours, and

the liquid was kept actively stirred during this time. The alkylation was thereafter continued for two hours at 30° and for five hours at 50°, the partly methylated product being finally extracted with boiling methyl alcohol. After filtration and evaporation of the solvent, a viscid, yellow syrup remained, which was only slightly acid, and contained very little resinous matter. The syrup was dissolved in alcohol, shaken with barium carbonate to remove acids, and decolorised with animal charcoal. The neutral residue left on evaporation of the alcohol was now partly soluble in the requisite amount of methyl iodide, complete solution being obtained by the addition of a little acetone. A second alkylation, conducted as already described and lasting over twelve hours, was carried out on this solution, the product being isolated and purified as before. In the final alkylations, which were carried out in methyl iodide solution, no oxidation took place, and the methylation was therefore conducted in the usual way. The final product was a yellow, mobile syrup, which, on standing, solidified completely to a mass of slender prisms. After drying on a tile and three crystallisations from methyl alcohol, the product melted at 132—134°.

In acetone solution, the following figures were obtained :

$$c = 3.024, l = 2, [\alpha]_D^{20} + 14.30^\circ, [\alpha]_D^{20} + 236.4^\circ$$

Analysis gave :

$$C = 61.68; H = 8.22.$$

$$C_{18}H_{25}O_5N \text{ requires } C = 61.74; H = 8.04 \text{ per cent.}$$

The compound is therefore tetramethyl glucosyanilide, identical with that obtained from tetramethyl glucose (w. p. 135°, $[\alpha]_D + 238.4^\circ$). The hydrolysis, which was carried out as usual, gave a good yield of tetramethyl glucose, melting at 87—88°.

Alkylation of Glucoseoxime.

The oxime, which was prepared by Wohl's method (*Ber.*, 1891, 24, 993), melted at 138° and showed in aqueous solution the downward mutarotation, $[\alpha]_D - 7.8^\circ \rightarrow -0.8^\circ$. Owing to the limited solubility of the compound in methyl alcohol, the addition of water was necessary in the first treatment with the alkylating mixture.

The oxime (1 mol.) was dissolved in water, a large excess of methyl iodide added, and sufficient methyl alcohol to effect complete solution. The addition of silver oxide (5 mols.) occasioned a brisk reaction, which was completed by six hours' heating on a water-bath. The product was extracted with boiling methyl alcohol, and, on removal of the solvent, a neutral, yellow syrup remained. This partly methylated product, after drying in a vacuum, was now freely soluble in methyl

alcohol, and consequently no water was necessary in the second and third treatments with the alkylating mixture. In the fourth methylation, the addition of very little methyl alcohol sufficed to effect complete solution of the product in the requisite amount of methyl iodide, and, in this case, ether was used as the extracting agent. The syrup was now distilled in a vacuum, after which it proved to be readily soluble in methyl iodide. Two final alkylations were then carried out in this solvent, after which the product was recovered and purified by fractional distillation under diminished pressure (b. p. 160—165° under 30 mm. pressure). The alkylated oxime was thus obtained as a colourless, neutral syrup, showing no action on Fehling's solution until vigorously boiled with the reagent.

Analysis gave :

C = 49.61; H = 8.71; OMe = 59.43.

$C_6H_8ON(O\cdot CH_3)_5$ requires C = 49.81; H = 8.68; OMe = 58.49 per cent.

The compound is therefore pentamethyl glucoseoxime. In composition, boiling point, and specific rotation, it resembled the mixture of stereoisomeric tetramethyl glucoseoxime methyl ethers prepared by the alkylation of tetramethyl glucoseoxime, and the identity of the two specimens was confirmed by a comparison of the optical changes undergone by each during hydrolysis. In parallel experiments, the specific rotations at first diminished and then increased at an equal rate to a constant value, which agreed closely with that calculated for tetramethyl glucose. This result seems to distinguish the alkylated oximes from a mixture of the α - and β -alkylated methylglucosides, which, during hydrolysis, show the reverse optical changes. On working up the product as usual, the syrup obtained crystallised readily, giving a good yield of tetramethyl glucose (m. p. 88—89°).

Mutarotation of Glucoseanilide.

As explained in the introduction, two forms of glucoseanilide exist, one dextro- and the other laevo-rotatory, and the conversion of the former into the latter gives rise to mutarotation. In preparing the compound by Sorokin's method, the first crops obtained displayed a dextrorotation in methyl-alcoholic solution, but in each case the optical rotation diminished on standing, and attained nearly the same constant values. The actual extent of these optical changes is shown below :

	Initial $[\alpha]_D^{20}$.	Final $[\alpha]_D^{20}$
Crop I.	+10.7	-52.3
II.	15.1	51.8
III.	-20.1	53.1

In determining the rotations, 3 per cent. solutions were used throughout, and, although the mutarotation was, even in the absence

of catalysts, complete in twenty-four hours, the solutions were in each case preserved for one hundred hours. The end values obtained in about twenty experiments in which mutarotation was observed were fairly uniform, the average value being $[\alpha]_D^{20} - 52.3^\circ$. These alterations in the rotatory power are without doubt due to stereochemical changes, as the analysis of dextrorotatory crops, and also of the products of constant levorotatory power obtained from them, showed that all the specimens had the composition of glucose-anilide.

The dextrorotatory variety is the less soluble form, and is the first product of the condensation of glucose and aniline. This was shown by the changes in rotation during the formation of the compound. A solution of 10 grams of glucose in 100 c.c. of ethyl alcohol was prepared and kept until it had attained the constant rotatory power. Twenty-seven grams of aniline were then added, and the solution maintained for three weeks at a temperature varying from $+2^\circ$ to $+6^\circ$. The changes of rotation observed in a 2-dm. tube are shown in the following table:

Time in days.	$[\alpha]_D^{20}$.	Time in days.	$[\alpha]_D^{20}$.
0	$+6.5^\circ$	7	$+6.5^\circ$
1	7.0	11	4.2
3	7.4	14	1.7
4	7.5	17	-0.25
5	7.1	18	1.50

The initial rise in the rotation indicates that the form first produced is more strongly dextrorotatory than glucose, the subsequent fall being due to the conversion into the levorotatory isomeride. On the analogy of the glucosides, the former may be termed β -glucoseanilide and the latter α -glucoseanilide.

Considering the relative rates of formation of the two isomerides, it follows that, during the hydrolysis of a mixture of α - and β -forms, the latter should be decomposed more rapidly than the former, and thus the optical rotation should at first diminish rapidly and then increase to a constant value. We have been unable to apply this hydrolytic method, however, as the addition of hydrogen chloride to a solution of dextrorotatory power, which contained both α - and β -forms, at once caused very rapid mutarotation, the permanent value being reached almost immediately, and before hydrolysis proceeded.

In such a case, the hydrolytic action of enzymes may be applied, but the polarimetric examinations of aqueous solutions of the anilide to which emulsin or maltase had been added showed that in each case the rate of hydrolysis did not differ in any marked degree from a control solution containing the anilide alone.

Evidence was, however, obtained that the anilide of constant

rotatory power is essentially one form. This view was supported by the fact that all attempts to separate, either by precipitation or partial solution, a specimen of the compound showing a higher laevorotatory power than -52.3° , but capable of mutarotation in the dextro-direction to this value, were unsuccessful. Again, on hydrolysing the solution of permanent rotatory power by heating with very dilute aqueous hydrogen chloride, the specific rotation increased rapidly and without fluctuation to a constant value. This regularity in the optical change is consistent with the idea that the value $[\alpha]_D - 52.3^\circ$ approximately represents the specific rotation of the pure α -form.

The effect of temperature on promoting the reversible change $\alpha \rightleftharpoons \beta$ cannot be demonstrated on the fused anilide, as the latter undergoes partial decomposition in the neighbourhood of the melting point. On heating methyl-alcoholic solutions of the pure α -form to 50° for several hours, the desired result was obtained, the specific rotation increasing in the dextro-sense:

Experiment.	Initial $[\alpha]_D$ at 20° .	$[\alpha]_D$ after heating to 50° .	End value on standing at 20° .
I.	$[\alpha]_D^{20} = 51.4^\circ$	$[\alpha]_D^{50} = 45.9^\circ$	$[\alpha]_D^{20} = 52.3^\circ$
II.	51.3	45.1	51.8
III.	5.0	45.7	52.0

In experiment III, the specimen contained both stereoisomeric forms, but, nevertheless, the same equilibrium point was reached at 50° . The fact that the subsequent mutarotations at 20° gave the normal end values shows, moreover, that the optical changes observed on heating are due to stereochemical alteration. The effect of heating the α -form was also shown by fusing the anilide with very little methyl alcohol at 100° . In this way, the decomposition usually undergone by the anilide in the fused state was avoided, and the specific rotation of the substance during this treatment was found to have altered from -52° to -10° , and, as usual, the product was once more capable of mutarotation to the initial value. The converse experiment in which dilute solutions of the α -form were cooled in ice and calcium chloride for several hours led to no result, the initial rotatory power remaining unaltered.

Relative Solubilities of α - and β -Glucoseanilides.

On extracting a mixture of the α - and β -forms with a large excess of boiling ethyl acetate, the bulk of the compound remained undissolved, but a small quantity passed into solution, and was readily obtained in the crystalline state. The treatment effected a partial separation of the two forms, excess of the α -variety passing into solution, and thus the rotation of the undissolved residue was more dextro-

rotatory than that of the specimen before treatment. Boiling with ether led to similar results. The magnitude of these changes is shown in the following table:

Extracting agent.	Time of boiling, hours.	Initial specific rotation of mixture.	Initial specific rotation of undissolved residue.
Ether	1	-20°	-5°
"	7	5	+16
Ethyl acetate	5	5	12
"	2	+15	24
"	2	14	24

Conversely, when concentrated alcoholic solutions of both forms were cooled, the crop which was first deposited contained a larger proportion of the β -form than was present in the original mixture. Thus a solution containing 9 per cent. of the mixed anilides showing a specific rotation of -8.7° , when cooled in ice, deposited a crop which showed the initial rotation $[\alpha]_D^{20} +10.7^\circ$. On the other hand, a solution showing the initial rotation -52.3° , when similarly treated, yielded a crop which naturally possessed the same rotatory power.

Effect of Catalysts in Promoting the Mutarotation.

When special precautions are taken to clean thoroughly the polarimeter tube and its accessories, the mutarotation of glucoseanilide in methyl-alcoholic solution is comparatively slow, the permanent rotation being observed, as a rule, after about twenty-four hours interval. The addition of a trace of hydrogen chloride, however, accelerates the change greatly, the mutarotation being complete in a few minutes; judging from the end values obtained, no hydrolysis or other decomposition occurred. The addition of small quantities of water to the solution had no appreciable effect in altering the rate of the optical changes, but traces of aniline retarded the process somewhat. Comparisons of the rate of optical change must in this case be accepted with caution, as we find that the most minute traces of hydrogen chloride have a pronounced effect in accelerating the transformation into the α -form.

Mutarotation of Glucoseanilide in Water.

Aqueous solutions of glucoseanilide display very rapid mutarotation, but a definite end value is not reached, owing to partial hydrolysis of the compound. As the anilide only dissolves slowly in water, a considerable time must elapse before the first polarimetric reading can be taken, and thus all the rotations determined in water were levorotatory. The following table shows the nature of these optical changes, and the catalytic effect of a trace of hydrogen chloride in promoting the change:

Initial Specific Rotation of the Specimen in Methyl Alcohol, $[\alpha]_D^{20} + 15.4$.

Solution I.		Solution II.	
$c = 2.873$.		$c = 3.127$.	
Time from contact of anilide with water, mins.	$[\alpha]_D^{20}$.	Time from contact of anilide with water, mins.	$[\alpha]_D^{20}$.
19	-28.7	15	-22.0
30	36.5	Added a trace of hydrogen chloride.	
40	41.0		
50	50.9		67.1
60	57.7		86.3
70	61.2		92.4
160	77.7	18	93.5
		30	85.1

In each case the levorotatory powers slowly diminished on further standing, and the solutions were then found to contain free aniline, showing that partial hydrolysis had occurred. The minimum value obtained in the case of solution II ($[\alpha]_D^{20} - 93.5^\circ$) probably approximates to the true value for the specific rotation of the equilibrium mixture in water, as only very slight hydrolysis could then have taken place.

Mutarotation of Tetramethyl Glucoseanilide.

As glucoseanilide and tetramethyl glucoseanilide have been shown to possess a similar structure, both compounds should be capable of mutarotation. In a previous paper, it was stated that we were unable to detect any change in the rotation of the latter compound in acetone solution. This observation we have confirmed, but find that in methyl-alcoholic solution slow, but extensive, changes can be observed.

The alkylated anilide was prepared by heating a concentrated solution of tetramethyl glucose in methyl alcohol with an excess (5 mols.) of aniline on a water-bath for two hours. The product crystallised readily on cooling the solution. On crystallising the compound several times from methyl alcohol, the specific rotation gradually increased, and finally, after eight recrystallisations, became constant. The value then found for a methyl-alcoholic solution was $[\alpha]_D^{20} + 224.0^\circ$, and a similar solution in acetone showed $[\alpha]_D^{20} + 238.4^\circ$. The alcoholic solution, on standing, showed downward mutarotation:

Time in hours.	Specific rotation in methyl alcohol.
0	$[\alpha]_D^{20} + 224.0$
24	203
36	190
48	178
60	162
72	150
84	135
108	105
	↓
	47 on addition of a trace of hydrogen chloride.

Solutions in acetone, when preserved for an equal time, showed no alteration in rotatory power. The addition of a trace of hydrogen chloride, however, promoted rapid mutarotation of both the acetone and methyl-alcoholic solutions, the permanent value in the latter case ($[\alpha]_D^{20} + 47^\circ$) being reached in from fifteen to twenty minutes. The anilide then present in the solution seems to be an equilibrium mixture of α - and β -forms, as on hydrolysis with 10 per cent. hydrogen chloride the specific rotation at first diminished about 20° below the equilibrium point, and then increased to the value for tetramethyl glucose. This indicates the presence of a form showing a very small dextro- or possibly a *laevo*-rotation, which is less readily hydrolysed than the strongly *dextro*-isomeride with which it is mixed. The latter, from its relative instability towards hydrolytic agents, would be the form first produced, and we therefore term it β -tetramethyl glucoseanilide. This brings the compound into line with the parent anilides as shown below :

<i>Glucoseanilide.</i>	<i>Tetramethyl glucoseanilide.</i>
α -Form. $[\alpha]_D - 52.3^\circ$. More soluble form ; less readily hydrolysed.	<i>Laevo</i> - or feebly <i>dextro</i> -rotatory. More soluble form ; less readily hydrolysed.
β -Form. <i>Dextrorotatory</i> . Less soluble form ; produced first and more readily hydrolysed.	$[\alpha]_D + 238.4^\circ$. Less soluble form ; more readily hydrolysed.

As pure tetramethyl glucoseanilide is stable at the melting point, the effect of fusion in causing the change $\beta \rightleftharpoons \alpha$ was studied. A specimen of the compound which originally gave $[\alpha]_D + 221^\circ$ showed, after fusion at 130° , $[\alpha]_D + 158^\circ$, isodynamic change in the direction $\beta \rightarrow \alpha$ had therefore occurred. At higher temperatures, the equilibrium point was still further displaced in the *laevo*-direction, the values $+68^\circ$ and $+56^\circ$ being obtained as the result of fusion for twenty minutes at 160° and 180° respectively.

The authors take this opportunity of thanking Professor Purdie for his interest in their work, and of expressing their indebtedness to the Carnegie Trust for a research grant.

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CXXXIX.—*The Use of the Micro-balance for the Determination of Electrochemical Equivalents and for the Measurement of Densities of Solids.*

By OTTO BRILL and CLARE DE BRERETON EVANS.

THE methods here described were worked out with the object of discovering the properties of what appeared to be an unknown metal, traces of which were found by one of us in thorianite (Evans, *Trans.*, 1908, 93, 667).

For the quantitative study of a substance of which only a few milligrams were available it was found necessary to develop new methods, which may prove to be of use also in the determination of the physical and chemical constants of other substances, such as some of the radio active elements, which are procurable only in very small quantity.

The balance used in this work was a modified and improved form of the Nernst quartz-fibre balance (Nernst, *Nachr. K. Ges. Wiss. Göttingen*, 1902, 2; and Brill, *Ber.*, 1903, 36, 2056). A description of this balance will be given elsewhere; it is sufficient here to state merely that it was possible to read to 0.02 of a division of the empirical scale corresponding with 0.004 milligram, appropriate corrections being made in the readings by means of a calibration curve. With such an instrument, the amount of material necessary for the determination of atomic weight or density is reduced to a fraction of a milligram.

Determination of Electrochemical Equivalents and the Measurement of Very Small Currents.

A current of a few milliamperes was passed through (1) a solution of silver perchlorate containing 2.5 grams of silver perchlorate per 100 c.c. (Carhart, Willard, and Henderson, *Trans. Amer. Electrochem. Soc.*, 1906, 9, 375), and (2) a solution of the metal to be investigated; these were connected in series. As cells, it was found convenient to use small porcelain crucibles the solution in each being kept stirred by the passage of a slow current of small bubbles of hydrogen. The cathodes, which were made of thin platinum foil, weighed from 5 to 10 milligrams, the area of each being about 0.02 sq. cm. A spiral of thin platinum wire answers very well for metals such as copper and silver, but a larger surface is advantageously employed for elements such as antimony which tend to form a less strongly-adherent deposit. After about twenty minutes the electrodes were withdrawn from the solutions and washed several times in pure water, the usual precautions being

observed; they were then dried by heating for five minutes in a steam-oven, cooled in a desiccator, and weighed again as quickly as possible.

The method was first tested by determining the electrochemical equivalent of copper which was deposited from a solution of the sulphate. The results of these experiments are given in table I; they show that it is possible to obtain a very fair value for the atomic weight of an element by using as little as one-third of a milligram provided the element obeys Faraday's law to the same extent as does copper.

TABLE I.

Weight of copper deposited in milligrams.	Weight of silver deposited in milligrams.	Equivalent of copper (Ag = 107.934).	Time in minutes.	Current in amperes.	
				Calculated from copper deposit.	Calculated from silver deposit.
0.5542	1.8135	32.84	20	0.00140	0.00135
0.3334	1.1545	31.16	25	0.000675	0.000689
0.6729	2.2754	31.91	25	0.001362	0.001357
0.9236	3.2410	32.21	30	0.001558	0.001520
1.0550	3.7233	31.48	30	0.001830	0.001851
0.8332	2.8018	32.10	30	0.00140	0.00139

Mean value = 31.95.

The unknown metal mentioned above appeared to be related to antimony, so this element was made the subject of the next experiment. Meanwhile the probability was not lost sight of that identical methods would be likely to succeed with antimony and bismuth, and therefore also with polonium, the atomic weight of which it is proposed to attempt to determine in the same way.

The difficulties connected with the determination of the equivalent of antimony arise chiefly from the tendency it shows to deposit from simple solutions of its salts in a black form which does not adhere firmly to the cathode. This defect was ultimately overcome by adding to a 0.5 per cent. solution of the chloride, acidified with hydrochloric acid, a trace of gelatin.* Under the influence of this colloid the deposit of antimony assumed a grey adherent character, even at the ordinary temperature as long as the current density remained at about 0.02 ampere. It was found later that by keeping the solution at a temperature of 70–80°, the current density might be considerably increased without risk of the black form appearing.

The electrochemical equivalent of antimony found by this method was 40.9, the amount of metal deposited in each of the two experiments the results of which were in close agreement being

* Patten and his collaborators have recently made use of the effect of colloids on electrolytic solutions to obtain a good deposit of lead (*Trans. Amer. Electrochem. Soc.*, 1906 to 1908).

about 0.5 milligram. It is noticeable that the numbers obtained by other observers are also somewhat higher than the theoretical value, which is 40.1 (Pfeiffer, *Annalen*, 1881, 209, 261; Popper, *Annalen*, 1886, 233, 153. For reasons of this discrepancy, see also Cohen, Collins, and Strengers, *Zeitsch. physikal. Chem.*, 1905, 50, 29).

It is obvious from the above considerations that the same method may be employed for measuring very small currents by means of a silver or copper micro-coulometer.* The last two columns of table I show that currents as small as half a milliampere can be measured in this way with a fair degree of accuracy, which is considerably increased by using both a silver and a copper micro-coulometer, these serving to control each other.

Determination of the Densities of Solids.

The micro-balance can also be used for the direct measurement of the specific gravity of solids which can be obtained in regular form; for example, a small crystal or a spherical globule of metal, &c. This is first measured in all its dimensions under the microscope and is then weighed on the micro-balance. In our experiments we employed a travelling microscope of low power, such as is used for measuring spectra, the volumes being calculated from the mean values obtained from a number of observations. If very accurate results are needed, crystals should be well formed with sharp edges, but it is often possible to simplify the calculation by using thin plates, by taking advantage of cleavage planes to get rid of facets, or even by cutting or filing the crystal into some elementary form.

Table II gives a list of substances chosen more or less at random and prepared with only ordinary care, the densities of which were determined in the way indicated. It will be seen that a very good approximation to the density of tin was obtained by using three small beads the aggregate weight of which amounted only to about half a milligram. Of the two crystals of diphenylene disulphide which were examined and which gave concordant results, the form of one was modified by cleavage, whilst corrections were made for imperfections in both crystals of nitroxylidine.

The advantages of this direct measurement of density over the methods now in use are obvious in the cases of rare, valuable, or very chemically active substances, such as many of the radioactive substances, and not a few organic compounds. Not only are all the errors attending the use of liquids eliminated, but the quantity

* Since these experiments were concluded, Prof. Rose and F. Comrat have described the use of a silver (nitrate) micro-coulometer for the same purpose (*Zeitsch. Elektrochem.*, 1908, 14, 86).

TABLE II.

Substance.	Form.	Volume in cu. mm.	Weight in milligrams.	Density at 18° compared with water at 4°.	Average density found.	
					By authors.	By other observers.*
Tin	1. Spherical bead, diameter 0.0202 mm.	0.12496	0.9243	7.399	{ 7.290	7.285 (Miller)
	2. Three spherical beads of diameters 0.2865, 0.3341, and 0.3312 mm.	0.06087	0.4370	7.180		7.373 (Deville)
Sodium nitrate, NaNO ₃	1. Rhomb (quadratic) crystallised from water	1.20234	2.6109	2.172	{ 2.175	2.188 (Marx)
	2. " " "	0.80417	1.7528	2.177		2.265 (Retgers)
Potassium ferrocyanide K ₄ Fe(CN) ₆ ·3H ₂ O	1. Plate (monoclinic) crystallised from water.	1.44515	2.4730	1.719	{ 1.723	1.833 (Thomson)
	2. " " "	0.47885	0.8219	1.717		1.880 (Schiff)
	3. " " "	0.51847	0.8842	1.734		
Copper formate, (H·CO ₂) ₂ ·Cu·4H ₂ O	1. Rhomb (monoclinic) crystallised from water	1.79656	3.0654	1.818	{ 1.812	1.831 (Schroeder) †
	2. " " "	0.58847	1.0624	1.805		
Barium chloride, BaCl ₂ ·2H ₂ O	Plate (rhombic) crystallised from water	0.94692	2.9265	3.090	{ 3.060	3.05 to 3.08
	1. Plate crystallised from alcohol	0.46088	0.78646	1.706		
Diphenylene disulphide	2. " " "	0.73391	1.25197	1.706	{ 1.706 ±	—
	1. Rhomb crystallised from alcohol	1.83486	2.40220	1.309		
6-Nitro- <i>m</i> -4-xyldine	2. " " "	1.46991	1.97750	1.345	{ 1.88 ±	—
	1. Rhomb crystallised from alcohol					

† Newly determined.

+ Ber., 1881, 14, 21.

* See Gmelin, *Handbuch der anorgan. Chem.* (new edition).

required for a determination is so small (about 0.5 milligram) that mere traces of metals, or elements such as sulphur, may be examined in this way if they are first caused to assume a sufficiently regular shape, by melting or otherwise. Such considerations lead also to the conclusion that there is in these small-scale determinations of density a means of identification which can be used in cases where, for the reasons already suggested, it is not allowable to employ chemical tests; indeed, this has already proved to be the simplest and most conclusive way of identifying small metallic beads isolated from thorianite in the course of analysis.

Lastly, this method may be of value from the point of view of the examination of optical isomerides (compare Auwers at the Congress of Applied Chemistry at Rome, 1906) and the calculation of topic parameters. For the latter purpose, there is at present only one way of determining the densities of crystals with sufficient accuracy, namely, Retgers' free suspension method (*Zeitsch. physikal. Chem.*, 1889, 3, 296), and this is, generally speaking, limited in its application to substances the specific gravity of which is below 3.6.* There is no such limit to this direct measurement method by means of which a high degree of accuracy might also be reached by examining a sufficient number of crystals of a given substance, the error due to weighing operations on the micro-balance being negligible.

Thanks are due to Sir William Ramsay and to Mr. N. T. M. Wilson for the interest they have taken in the work.

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CXL.—*The Fluorescence of Platinocyanides.*

By LEONARD ANGELO LEVY.

NEARLY all platinocyanides exhibit the phenomenon of fluorescence to a very marked degree; as a class, they are unique in this property. Stokes (*Phil. Trans.*, 1853, 143, 396) appears to have been the first to note the remarkable optical characters of these salts. He observed that platinocyanides exhibited a powerful fluorescence when stimulated by ultra-violet light. The compounds examined by him include the magnesium, potassium, barium, calcium, strontium, and lithium compounds. He noticed that the majority of the amorphous platino-

* See Groth's *Introduction to Chemical Crystallography*.

cyanides of the heavy metals were non-fluorescent, but that the mercuric salt formed an exception and exhibited a strong yellow fluorescence. Stokes also observed that the fluorescence was a characteristic of the solid salts, and that their aqueous solutions were colourless and non-fluorescent.

Apart from these researches of Stokes, undertaken in the course of a general investigation on fluorescence, very little indeed has been done, and the author was accordingly led to attempt the elucidation of the subject: experiments have so far been made with the object of determining what effects such conditions as purity, state of hydration, basic radicle, &c., exert on the character of the fluorescence.

In the course of the investigation, several new platincyanides have been prepared. These include the hydrazine, hydroxylamine, uranyl, 1:4-diphenyl-3:5-*endo*-anilo-4:5-dihydro-1:2:4-triazole (nitron), and guanidine salts. Some of these substances exhibit interesting properties, and have already been described (*Trans.*, 1906, 89, 125; *Proc. Camb. Phil. Soc.*, 1907, 14, 159).

EXPERIMENTAL.

Two sources of radiation were used to excite the fluorescence, namely, (i) the ultra-violet light from an induction spark between iron electrodes, and (ii) the radiation from a small amount of radium bromide.

It was found necessary to have some method of comparing the intensities of the fluorescence exhibited by various specimens in order to assign a numeral value to each intensity.

A crystal of the platincyanide, the fluorescence of which is to be investigated, is placed in a tray of black paper and viewed by a short focus lens. A small quantity of radium bromide, placed under the tray, is gradually removed until the fluorescence of the crystal is only just perceptible in the dark. The distance between the radium bromide and the crystal is measured. Assuming that the intensity of the rays varies inversely as the square of the distance, the intensity of fluorescence is proportional to the square of the distance between the radium bromide and the crystal. In the following experiments, the intensity of the fluorescence of a certain specimen of barium platincyanide is arbitrarily fixed at 100, and thus proportional values are assigned to the other compounds examined. (The foregoing method of comparison is similar to that adopted by Beilby, *Proc. Roy. Soc.*, 1905, 74, 506.) The method is not exact, but it yields an approximate value, which is sufficient.

I. Barium Platinocyanide.

This salt was prepared by passing gaseous hydrocyanic acid into a pasty mixture of one part of platinum dichloride, one and a-half parts of freshly-precipitated barium carbonate, and five parts of water kept nearly boiling. The gas was passed through until all effervescence ceased, the solution then being boiled and filtered hot. A solution of barium chloride and barium platinocyanide, $\text{BaPt}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$, was thus obtained, the latter being deposited on cooling in golden-yellow, transparent crystals exhibiting a purple sheen. The crystals often show red and green colours on the edges, this effect being especially noticeable when they are immersed in water. The fluorescence exhibited under ultra-violet light or radium is feeble.

A marked difference is produced in the appearance of this salt and in the intensity of the fluorescence which it exhibits on recrystallisation from water to which small amounts of various foreign substances have been added.*

(a) A solution of 1 gram of the yellow crystals in 10 c.c. of water was crystallised with 0.1 gram of the following substances:

Substance.	Colour of crystals.	Fluorescence.
Potassium cyanide	green	41
Hydrocyanic acid (no exact quantity)	lemon-yellow	20
Potassium ferrocyanide	lemon-yellow	26
Potassium sulphocyanide	lemon-yellow	26
Cyanogen (gas passed into the hot solution) ...	lemon-yellow	26*
Potassium silver cyanide	lemon-yellow	23
Mercuric cyanide	golden-yellow	5
Cyanogen iodide	golden-yellow	5
Barium cyanide	green (most marked)	100

In order to account for the production of the green from the yellow salt, the following suggestions, amongst others, have been considered. The determining factor may be the presence of: (i) *Potassium ions*. This supposition is supported by the fact that some potassium salts will effect the change. (ii) *Barium ions* are, for the same reason as potassium ions, indicated as a possible cause. (iii) *Hydroxyl ions*. This hypothesis is supported by the following facts: (a) Ionised cyanides are very efficient in producing the change. These salts are all more or less hydrolysed by water, yielding hydrocyanic acid and

* During the progress of these investigations, the author's attention was called to a statement by Brochet and Petit (*Ann. Chim. Phys.*, 1903, [viii], 3, 433). They prepared barium platinocyanide by electrolysis of a solution of barium cyanide between platinum electrodes, using an alternating current. The salt obtained is described by them as yellow, slightly dichroic, and very slightly fluorescent under the action of radium. They state that this product becomes fluorescent if crystallised with barium cyanide. They analysed the two products, and state that they both have the same composition, but give very few figures in support of their analyses.

M + OH'; (b) non-ionised cyanides produce no effect; (iv) *Cyanogen ions*. This hypothesis is suggested by the following facts: (a) Substances yielding cyanogen ions have a very great effect; (b) non-ionised cyanides, for example, mercuric cyanide and cyanogen iodide, have no effect; (c) substances yielding few cyanogen ions, for example, potassium ferrocyanide and potassium thiocyanate, produce a slight change.

0.5 Gram of yellow barium platinocyanide was crystallised with 0.1 gram of the following substances:

Salt.	Colour of crystals.	Fluorescence.
Potassium chloride	yellow	8
Potassium nitrate	yellow	8
Potassium acetate	lemon-yellow	11
Barium chloride	yellow	8
Barium nitrate	yellow	8
Barium acetate	lemon-yellow	11

Two c.c. of a solution of yellow barium platinocyanide (25 grams per 100 c.c.) were crystallised with 1 c.c. of an *N*/100 solution of various alkalis.

Substance.	Colour of crystals.	Fluorescence.
Ammonium hydroxide	lemon-yellow	21
Methylammonium hydroxide	lemon-yellow	24
Dimethylammonium hydroxide	lemon-yellow	26
Trimethylammonium hydroxide	lemon-yellow	24
Tetramethylammonium hydroxide	lemon-yellow	30
Sodium hydroxide	lemon-yellow	23
Barium hydroxide	green	100

It appears from the above results that alkalis are efficient in producing the change from yellow to green. The effects obtained with barium and potassium acetates may be explained by the slight hydrolysis and resulting alkalinity of aqueous solutions of these salts.

Effect of Cyanogen Ions.—It was found that only a very slight trace of barium cyanide was required to determine the deposition of the very green, fluorescent crystals. This substance and barium hydroxide are the most efficient in effecting the change. There is no simple method of deciding whether the effect produced by barium cyanide is occasioned by the cyanogen ions or by the hydroxyl ions produced by hydrolysis. If the effect is due to cyanogen ions, potassium cyanide should be equally efficient (as barium ions have been proved to be inactive), whereas this is not the case.

Varying quantities of barium cyanide were used, but in every case the crystals deposited were similar.

(b) The green crystals, obtained by crystallising with barium cyanide, were recrystallised with small amounts of the following substances:

Substance.	Colour of crystals.	Fluorescence.
Hydrochloric acid	yellow	8
Tartaric acid	yellow	11
Acetic acid	yellow	11
Hydroplatinocyanic acid ...	golden-yellow (most marked effect)	3

The transition from the green to the yellow variety is probably determined by the presence of hydrogen ions. This hypothesis is supported by the following facts: (i) Acids determine the deposition of yellow crystals from a solution of the green salt; (ii) weak acids, for example, carbonic acid, have but little effect; (iii) hydroplatinocyanic acid is the most efficient.

Nature of the Green and Yellow Modifications.—The differences between the two varieties of barium platinocyanide may be due to various causes, amongst which the following appear to be most worthy of consideration: (a) The formation of a small amount of double salt; (b) a difference in crystalline form or habit; (c) there may be a difference in chemical composition; (d) the two varieties may be isomeric forms* of the same substance.

(a) *The Formation of a small amount of Double Salt or Mixed Crystal.*—The production of the green salt may be due to a small amount of double decomposition, whereby a little potassium platinocyanide is formed. The pure platinocyanide may be only very slightly fluorescent, and may only exhibit this property to any extent when another platinocyanide is present in solid solution. This is an analogy for this behaviour in the case of the phosphorescent sulphides. The effect of barium cyanide and barium hydroxide cannot, however, be thus explained. The following experiments were made to test this hypothesis.

0.4 Gram of yellow barium platinocyanide was dissolved in water and a small quantity of magnesium sulphate was added. The amount of the latter was such that it would yield approximately 1/50th by weight of magnesium platinocyanide. The precipitated barium sulphate was filtered off. Similar experiments were made using sodium and potassium sulphates.

Sulphate used.	Quantity.	Colour of salt deposited.	Fluorescence.
Magnesium	0.006 gram	yellow	11
Sodium	0.006 „	yellow	11
Potassium	0.004 „	yellow	13

The above results, together with the fact that barium hydroxide and barium cyanide are so efficient, appear to indicate that the production of the green crystals is not due to the formation of a small amount of double salt or mixed crystal.

(b) *Crystalline Character of the Two Modifications.*—With the view of testing whether the crystals of the two varieties showed any difference in their crystallographic characters, Professor Lewis kindly

* The term "isomeric modification" is employed to indicate the existence of two varieties of the same chemical composition, but differing in some, but not necessarily all, of their physical properties.

measured the angles of the two modifications, and the following is his report:

"The crystals of the two varieties of barium platynocyanide are identical crystallographically, and the angle of extinction in the plane of symmetry is in both cases very nearly in the direction of the longest edge, which is selected in all descriptions as the vertical axis.

"The system is oblique, and the forms present are the same as those given by previous observers: 010, 110, 100, 011. The faces (010) show a purple fluorescence, the terminal faces (011) a green fluorescence. • •

"Taking the mean of the most trustworthy measurements, the elements are:

$$\beta = 76^{\circ}25'.$$

$$a : b : c = 0.4779 : 1 : 0.8678.$$

	Golden-yellow.	Green.	Calculated.
{100 : 110	39°57' or 40°25'	39°51' or 40°12'	40°9
{110 : 010	49 58	49 48 or 50 8	49 51
{010 : 011	64 10	65 9	65 5
{011 : 011	49 50	49 36	49 50
{110 : 011	—	64 4	64 15
{110 : 011	83 50	84 12	83 45
{100 : 011	77 53	77 35	77 42
{100 : 011	102 21	102 25	102 18"

This report clearly shows that the differences cannot be due to a difference of crystalline character, a conclusion which is further borne out by the results obtained by growing a crystal of one form in a solution of the other variety. Thus when a green crystal was grown in a solution of the yellow salt, the yellow salt was deposited, and when a yellow crystal was grown in a solution of the green salt, the green salt was deposited.

(c) *A Difference in Chemical Composition.*—The following experiments were undertaken in order to test this hypothesis: (i) The green salt was recrystallised many times from pure water, but no change in the colour and fluorescence could be detected, and no change is produced in the yellow crystals by recrystallisation from warm water. (ii) A solution of the green salt carefully tested for cyanide yielded negative results. (iii) A current of carbon dioxide was passed into a solution of the green salt. The escaping gas was passed into dilute potassium hydroxide, and the latter was then tested for cyanide. This experiment yielded only negative results. (iv) Tartaric acid was added to a solution of the green salt. Air was drawn through the solution, and passed into dilute potassium hydroxide, the latter being then tested for cyanide. No trace could be detected.

(v) Aqueous solutions of both varieties are quite colourless.

(vi) *Analysis of the two varieties.*

The percentage of barium in the two varieties was estimated by the usual method, using every precaution to secure an accurate result.

(a) *Yellow Salt.*

- (i) 0.7689 gave 0.3496 BaSO_4 . Ba = 26.9.
 (ii) 0.4652 „ 0.2116 BaSO_4 . Ba = 26.8.
 (iii) 0.4467 „ 0.2038 BaSO_4 . Ba = 26.9.

(b) *Green Salt.*

- (i) 0.4727 gave 0.2156 BaSO_4 . Ba = 27.
 (ii) 0.4545 „ 0.2070 BaSO_4 . Ba = 26.8.
 (iii) 0.4558 „ 0.2084 BaSO_4 . Ba = 26.9.
 $\text{BaPt}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ requires Ba = 27 per cent.

The two varieties are therefore identical in composition.

(d) *The Existence of Isomeric Modifications of the Salt.*

(i) 0.3 Gram of the yellow crystals was placed in a weighing bottle with 1 c.c. of water and 0.5 c.c. of an *N*/100 solution of ammonia, various amines, and sodium hydroxide. In one experiment, 1.5 c.c. of distilled water was added. The bottles were stoppered and heated on a water-bath for some time, nearly to boiling. The crystals deposited were in every case green, even when only pure water was used. This result apparently contradicts those already obtained; it can, however, be explained on the results of the experiments immediately described.

(ii) Some of the green and yellow crystals were heated to 100° in sealed glass capillary tubes.

Crystals used.	Colour after heating.	Fluorescence after heating.
Yellow	yellowish-green	improved
Green	green (crystals duller)	unaltered
Yellow and trace of water	green	strong

(iii) Specimens of the green and yellow crystals were heated with a few c.c. of water in sealed tubes to various temperatures.

Substance heated with water.	Tube.	Temp.	Colour of crystals deposited.	Fluorescence.
{ Yellow crystals	soft glass	110°	green	strong
{ Yellow crystals	soft glass	150	very green	intense
{ Yellow crystals	silica	110	yellow	feeble
{ Green crystals	silica	110	green	good
{ Yellow crystals	silica	170	yellow	feeble
{ Green crystals	silica	170	yellow	feeble

On heating green or yellow crystals with water to 170° in sealed silica tubes, the crystals deposited on cooling are nearly identical in colour and fluorescence.

(iv) Equal weights (0.2 gram) of the green and yellow modifications were dissolved in 2 c.c. of water to which 5 c.c. of absolute alcohol were added. The addition of equal quantities of ether to each caused the precipitation of the platino-cyanide. Both specimens gave a deposit of green powder. The two deposits were indistinguishable from each other in colour.

Substance.	Fluorescence.
Original yellow crystals	3
Original green crystals	100
Powder from green variety	7
Powder from yellow variety	8

(v) The above experiments indicate the existence of isomeric modifications; it was therefore of interest to see if the two varieties differed in density. The crystals were weighed in air and in chloroform on platinum pans supported by platinum wire. They were weighed in one pan in air, and then carefully transferred to the lower pan. Errors due to entangled air were avoided, as far as possible, by immersing the crystals in chloroform and exhausting to about 20 mm. pressure. The temperature of the chloroform was in every case 17°.

The following values for the density were obtained:

Yellow.		Green.	
2.076	2.077	2.085	2.087
2.076	2.073	2.085	2.082
2.078		2.086	2.080

It appears from these results that there is a small difference in the densities of the crystals, and that the green variety is the denser, but further observations are necessary to establish this.

The foregoing experiments favour the view that barium platino-cyanide exists in two isomeric modifications. These differ markedly in colour and fluorescence; their densities differ, but their crystalline characters are identical. Piperidine, which is well known to act as an isomerising agent in many instances, causes the conversion of the yellow crystals into the green form, and is very efficient—far more so than would be expected from its behaviour as a base. Experiments with colloidal platinum yield negative results.

The green variety appears to be the more stable at the ordinary temperature, but, on heating to a higher temperature, both modifications are deposited in an intermediate form which is much more closely allied to the yellow variety. It also appears that the deposition of the yellow salt is determined by the presence of hydrogen ions, and that of the green compound by the presence of hydroxyl and possibly cyanogen ions. The results obtained in glass tubes may be explained by the action of the alkali extracted from the soft glass. Support to this theory is afforded by the identity of the

products after precipitation by ether from the alcohol and water solutions, and by the minuteness of the quantity of cyanide required.

The points of difference may be tabulated :

A.		
Colour	Golden-yellow	Apple-green
Formation	(i) Determined by the presence of hydrogen ions	(i) Determined by the presence of hydroxyl or cyanogen ions
	(ii) Favoured by a higher temperature	(ii) Favoured by a lower temperature
Fluorescence	Poor (3)	Very intense (100)
Density	2.076	2.085
Crystalline character ...	} Identical	} Identical
Chemical composition ..		

The results of the foregoing experiments rendered it a matter of interest to ascertain whether a similar difference in modification was exhibited by crystalline platinoeyanidos other than the barium salt. The following experiments were accordingly made.

II. Calcium Platinoeyanide.

This salt was prepared by boiling a suspension in water of the calculated quantities of calcium oxide and copper platinoeyanide until the decomposition was complete. The liquid was then filtered and evaporated to a fairly small bulk, the calcium platinoeyanide being allowed to crystallise out. The following experiments were made to determine the effect (if any) of foreign substances on the colour and fluorescence of the salt deposited.

(a) A solution of one gram of calcium platinoeyanide in 10 c.c. of water was recrystallised with 0.1 gram of the following substances :

Substance.	Colour of crystals.	Fluorescence.
Hydrochloric acid	yellow	21
Sodium hydroxide	leaf-green	59
Potassium cyanide	leaf-green	39
Piperidine	leaf-green	30

(b) Portions of the green and yellow modifications of calcium platinoeyanide were heated with a little water in sealed tubes to various temperatures. The results obtained are tabulated below :

Crystals used.	Tube.	Temp.	Colour of crystals deposited.	Fluorescence.
{ Yellow	silica	100	yellow	poor
{ Green	silica	100	greenish-yellow	strong
{ Yellow	silica	160	yellow	poor
{ Green	silica	160	yellow	poor
Yellow	soft glass	160	green	strong

(c) *Crystalline character of the two modifications.*

Professor Lewis kindly measured the angles of the two varieties of the salt, and furnished the following report:

"Two varieties of calcium platinocyanide, differing in fluorescence, exist, which show no distinction in habit, forms, or angles. The one may be described as golden-yellow with green fluorescence on the pyramid faces; the other shows a green fluorescence on all faces, and this is very intense on the tops.

"The crystals belong to the prismatic system, and have long prism and pinakoid faces. The pyramidal faces are occasionally developed so as to give an oblique aspect, but the extinction is in both varieties parallel to the prism edge.

"The elements derived from measurements of two crystals of the green variety and one of the yellow kind are

$$a:b:c=0.9010:1:0.3506.$$

"Those given by Grailich are 0.90:1:0.3365.

"The forms observed on the yellow crystals are $a=\{100\}$, $p=\{120\}$, $o=\{111\}$, and on the green ones the same, together with $b=\{010\}$ and $t=\{211\}$. The table gives the angles observed and computed."

	Golden-yellow.	Green.	Calculated.
$\{a:m=100:110$	—	—	42°3'
$\{a:p$	60°53'	60°59'	*61 0
$\{p:b$	29 0	28 59	29 0
$\{p:p_1$	58 11	57 59	58 0
$\{p:o=120:111$	63 57	63 56	*64 0
$\{o:p_{11}$	115 57	115 58	116 0
$\{p_1:o$	84 0	84 2	83 59
$\{o:p_{211}$	95 45	95 50	96 1
$\{b:o=010:111$	—	71 53	71 53
$\{o:o_{111}$	—	36 14	36 14
$\{a:o$	69 41	—	69 51
$\{a:o_1$	40 17	—	40 18
$o:o_{11}$	55 15	—	55 16

The above experiments indicate that calcium platinocyanide can, like the barium salt, be obtained in two modifications of identical crystalline character. A comparison of their properties is appended in the following table:

	A.	B.
Colour	Pale yellow	Leaf-green
Formation	(i) Determined by the presence of hydrogen ions	(i) Determined by the presence of hydroxyl or cyanide ions
	(ii) Favoured by a low temperature	(ii) Favoured by a higher temperature
Fluorescence	Poor (21)	Intense (58)
Crystalline character...	Identical	

Drawing an analogy from the barium salt, it is probable that the two varieties are isomeric modifications.

III. Cerium *Platinocyanide*.

The calculated quantities of cerous sulphate and barium platinocyanide were mixed together in aqueous solution, and the resulting cerium platinocyanide was allowed to crystallise out. Separate portions of the salt so obtained were recrystallised from solutions to which traces of the following substances were added :

(a)	Substance added.	Colour of crystals.	Fluor. escence.
None	yellow	21
Hydrochloric acid	yellow	21
Potassium cyanide (slight precipitate was filtered off)	greenish-yellow	34
Sodium hydroxide (slight precipitate was filtered off)	greenish-yellow	37

(b) Separate portions of the two kinds of crystals were heated with water in sealed silica and glass tubes. Satisfactory results were not obtained, owing to a slight decomposition of the salt and the production of a white precipitate. Cerium platinocyanide evidently exhibits to a certain extent the phenomena displayed by the barium and calcium salts.

IV. Magnesium *Platinocyanide*.

This salt was prepared by double decomposition between the calculated quantities of magnesium sulphate and barium platinocyanide. Portions of the salt so obtained were crystallised from solutions containing traces of various foreign substances, namely, hydrochloric acid, potassium cyanide, and sodium hydroxide. The crystals obtained were always red with a green metallic reflection, and none of the specimens exhibited any fluorescence under the action of radium.

These experiments afford no evidence of the existence of more than one modification of the salt. Possibly some lower hydrate, such as $\text{MgPt}(\text{CN})_4 \cdot 5\text{H}_2\text{O}$, which is yellowish-green and fluorescent under radium rays, may be capable of existing in two forms differing in colour and fluorescence.

V. Thorium *Platinocyanide*.

Portions of this salt were recrystallised from solutions containing traces of hydrochloric acid, potassium cyanide, and sodium hydroxide. The crystals deposited were the same as those originally used, all the specimens having a fluorescence value of 8.

No evidence of the existence of more than one modification of thorium platinocyanide could be obtained from the foregoing results. Separate portions of the salt were heated with water in sealed silica and glass tubes. No satisfactory conclusions could be arrived at, owing to a partial decomposition taking place with the production of a white substance.

Radium-barium Platinocyanide.

As the majority of platinocyanides fluoresce under the action of the radiations from radioactive substances, the preparation of platinocyanides of the latter should prove of special interest. The radium salt should be self-luminous, and an investigation of its fluorescent properties might throw some light on the origin of the fluorescence conferred by the platinocyanide group on its salts.

Preliminary experiments having shown that barium platinocyanide is readily obtained from silver platinocyanide and barium chloride, this method of preparation was adopted for obtaining the radium-barium salt.

0.0655 Gram of radioactive barium chloride (activity about 1000) was dissolved in water and the solution was boiled with excess of silver platinocyanide. The silver salts were filtered off, and the remaining clear solution was allowed to crystallise in a desiccator.

The crystals, which were deposited last, were well-formed and red in colour. They were brightly luminous immediately after their preparation, but the intensity of their luminosity gradually diminished, and the red tint deepened in colour correspondingly. These effects are almost certainly due to the well-known alteration of barium platinocyanide by the radiations from radium compounds and the consequent reduction in the intensity of the fluorescence exhibited by this salt (Beilby, *loc. cit.*). The crystals finally showed a dirty green colour by transmitted light and a strong purple reflection: their luminosity was feeble.

The salt recovers its original properties on recrystallisation, and the luminosity which it exhibits in the presence of its saturated solution is considerably greater than that shown by the dry salt. This effect is in all probability due to the action of the water present in preventing the alteration of the platinocyanide.

The luminosity of the freshly-prepared radium-barium platinocyanide was compared with that of a mechanical mixture of radioactive barium chloride and barium platinocyanide. The relative amounts of the constituents of the mixture were chosen so as to approximate in composition as closely as possible to the compound. Both the mixture and the compound were carefully powdered. It was found that the compound was considerably more luminous than the mixture, and that the addition of a drop of water to each did not affect their luminosities.

Considering the small amount of radium which was actually present—less than 0.05 per cent.—the luminosity of the radioactive platinocyanide was remarkably intense.

Influence of the State of Hydration on the Fluorescence.

A conspicuous property of platinocyanides as a class is that of forming several variously coloured hydrates. It was of interest to ascertain whether each hydrate exhibits the property of fluorescence to the same degree, and to determine as far as possible in what way the fluorescence depends on the state of hydration.●

The following method was employed: A slow current of dry air was passed over a weighed quantity of platinocyanide contained in a glass tube drawn out to a capillary at each end. The current of air was continued, the salt being warmed, if necessary, until a definite colour change occurred. The tube was then sealed off at both ends and weighed, and the composition of the residual hydrate calculated from the loss of weight. ●

As it was not possible to guarantee the definite character of the product so obtained, a trial experiment was made to ascertain if this was likely to invalidate the results. A known weight of the non-fluorescent dihydrate of barium platinocyanide was mixed with 1 per cent. of the very fluorescent green tetrahydrate. The fluorescence of the mixture was found to be imperceptible. It is unlikely that as much as 1 per cent. of the higher hydrate would really remain, and hence the results obtained are considered trustworthy.

Since in these experiments it was necessary to examine the hydrates contained in glass tubes, the fluorescence was excited by means of radium radiations. The results obtained are set forth in the table appended:

Barium Salt.

Composition of hydrate.	Colour of hydrate.	Fluorescence.
BaPt(CN) ₄ ·4H ₂ O.....	golden-yellow	poor
BaPt(CN) ₄ ·4H ₂ O.....	green	very intense
BaPt(CN) ₄ ·2H ₂ O.....	brick-red	none
BaPt(CN) ₄	white	feeble

Strontium Salt.

SrPt(CN) ₄ ·5H ₂ O.....	white	strong
SrPt(CN) ₄ ·5H ₂ O.....	mauve	feeble
Indefinite.....	beetle-green	none
SrPt(CN) ₄ ·2H ₂ O.....	orange	none
Indefinite.....	yellow	none
Indefinite.....	red	none
SrPt(CN) ₄	white	very feeble

Calcium Salt.

CaPt(CN) ₄ ·6H ₂ O.....	leaf-green	very intense
Indefinite.....	brick-red	poor
CaPt(CN) ₄	white	feeble

Magnesium Salt.

Composition of hydrate.	Colour of hydrate.	Fluorescence.
$\text{MgPt}(\text{CN})_4 \cdot 7\text{H}_2\text{O}$	red with green reflection	none
$\text{MgPt}(\text{CN})_4 \cdot 5\text{H}_2\text{O}$	yellowish-green	strong
$\text{MgPt}(\text{CN})_4 \cdot 2\text{H}_2\text{O}$	white	none
$\text{MgPt}(\text{CN})_4$	orange	none

Uranyl Salt.

$(\text{UO}_2)\text{Pt}(\text{CN})_4 \cdot 4 \text{ or } 5\text{H}_2\text{O} (?)$...	metallic-green	none
Indefinite	yellow	none
$(\text{UO}_2)\text{Pt}(\text{CN})_4 (?)$	dull yellow	none

Yttrium Salt.

$\text{Yt}_2[\text{Pt}(\text{CN})_4]_3 \cdot 21\text{H}_2\text{O}$	red	none
Indefinite	yellow	none
$\text{Yt}_2[\text{Pt}(\text{CN})_4]_3 \cdot 14\text{H}_2\text{O} (?)$	white	none
$\text{Yt}_2[\text{Pt}(\text{CN})_4]_3 \cdot 4\text{H}_2\text{O} (?)$	orange	none

These experiments appear to indicate that generally only one hydrate exhibits the property of fluorescence to any extent. The luminosity, if any, exhibited by the other hydrates is very feeble. Some anhydrous platinocyanides are fluorescent, but others show no trace of this property. The anhydrous salts derived from the green and yellow modifications of the barium platinocyanide tetrahydrate are equally fluorescent. It is impossible to compare the intensities of the fluorescent light by the methods described above, and the table merely gives a visual estimate.

Spectroscopic Examination of the Fluorescence.

The ultra-violet light from an induction spark between iron poles was the source of radiation employed to excite the fluorescence. The secondary terminals of a large induction coil were connected to a large Leyden jar and the latter was joined up to the spark gap. The latter consisted of two wire nails passed through corks at each end of a glass tube, the side of which was blown out opposite to the spark. The light was passed through a narrow slit, then dispersed by two quartz prisms, and focussed by two quartz lenses. The visible part of the spectrum so produced was cut off by a screen. By these means the platinocyanide was illuminated by ultra-violet light only. The apparatus was arranged so that the table bearing the spark-gap and prisms could be revolved; thus various portions of the ultra-violet spectrum could be directed on to the platinocyanides. The fluorescence was observed by a spectrometer.

As the platinocyanide was illuminated by the light of its own

fluorescence only, the total visible spectrum could only be due to this light, and no visible scattered light could enter the spectrometer. The platino-cyanides were used in the form of large crystals when obtainable; otherwise, a "screen" of small crystals was prepared on a piece of glass coated with a thin layer of Canada balsam.

The spectra of the fluorescence are all similar in character, and consist in each case of a single band with ill-defined boundaries. The bands vary in position and extent, and no trace of any line spectra can be observed.

The following observations were made, the spectra being observed visually. Owing to the lack of definition of the boundaries of bands, the figures given are only approximate:

Platino-cyanides used.	Extent of band in wave-lengths.	Position of maximum intensity.
Lithium	6150—5260	orange-yellow
Sodium	5900—5100	yellow
Potassium	5400—4450	blue
Rubidium	5300—4375	blue
Cesium	5400—4150	indigo
Ammonium	5900—4880	green
Lithium rubidium (double salt)	6150—4850	green
Calcium	5475—4590	blue
Strontium	5550—4220	indigo
Barium (green form)	5675—4850	green
Barium (yellow form)	5650—4850	green
Magnesium	{ luminosity too faint to measure }	{ orange
Yttrium	5900—4400	orange
Erbium	5950—5100	orange
Thorium	5600—4650	greenish-blue
Thallium	No fluorescence exhibited	
Uranyl	No fluorescence exhibited	

An inspection of the above results reveals certain regularities.

(a) *Alkali Metals*.—(i) The position of maximum intensity of the band moves towards the violet end of the spectrum with increase of atomic weight.

(ii) The inferior limit of the band (that is, that end which is nearer to the red end of the spectrum) moves regularly up the spectrum towards the violet end.

(iii) The superior limit of the band also moves regularly up the spectrum with increase of atomic weight.

(b) *Alkaline Earths*.—(i) No regularity is displayed in the position of maximum intensity of the band. It is nearer the violet end of the spectrum in the case of the strontium salt than in the case of either the calcium or barium salts.

(ii) The inferior limit of the band moves regularly down the spectrum towards the red end with increase of atomic weight.

(iii) The superior limit of the band moves down with increase of

atomic weight in the case of the calcium and barium salts, but the strontium band has its superior limit nearer to the violet than the limit of the calcium band.

There are many parallels for this opposite behaviour on the part of the salts of the alkali metals and those of the alkaline earths.

It will be noticed that the double lithium-rubidium salt gives a band which starts from the inferior limit of the lithium band, but does not show the full extent of the rubidium spectrum.

The spectrum yielded by ammonium platinocyanide is intermediate in extent between the spectra of the sodium and potassium salts. This does not accord with the normal behaviour of ammonium salts with regard to their physical characters. In the majority of these, ammonium comes immediately after rubidium.

The spectra yielded by the two modifications of barium platinocyanide are identical in character and differ only in intensity.

The author is indebted to Professor Liveing for his assistance in this line of the investigation.

Conclusions.

(a) The mode of preparation of certain platinocyanides exerts a great influence on the intensity of the fluorescence exhibited. Some of these exist in two modifications having the same crystalline form, either of which can be obtained at will according to the method of preparation employed. The two varieties show a remarkable difference in their optical characters, differing in colour and very greatly in the intensity of the fluorescence which they exhibit (compare *Proc. Camb. Phil. Soc.*, 1908, 14, 378).

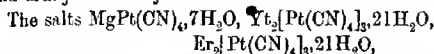
Of the compounds examined, the barium and calcium salts show this property most distinctly; the cerium salt exhibits it to a small extent only. Other platinocyanides which were examined showed no sign of this phenomena.

(b) The property of fluorescence of a platinocyanide under the stimulus of radium radiations is usually exhibited in a marked degree by one hydrate in particular; the others usually exhibit a feeble fluorescence or else show none whatever. The anhydrous salt is often non-fluorescent. It is worthy of note that, whereas the common red heptahydrate of magnesium platinocyanide shows no sign of fluorescence under radium radiations, the yellowish-green pentahydrate is strongly fluorescent.

(c) Experiments have been made to determine what effect, if any, the molecular weight of the basic radicle exerts on the character of the fluorescence. The preparation of a series of platinocyanides, of which the molecular weight of the bases increase homologously by equal increments such as CH_2 , should throw some light upon this ques-

tion. A suitable series of salts has not yet been obtained. The substituted ammonium salts do not yield a series of well-crystallised definite salts so necessary for the satisfactory estimation of the fluorescent properties.

The majority of platino-cyanides fluoresce under the stimulus of radium radiations, but some of these salts show no sign of this property. Amongst these the magnesium, erbium, yttrium, thallium, and uranyl salts may be mentioned.



are very similar in appearance and in the character of the fluorescence which they exhibit. All three occur in the form of bright red crystals, showing a brilliant metallic-green reflexion. Each of these displays an orange fluorescence of feeble intensity when stimulated by ultra-violet light, and all entirely fail to respond to the action of radium radiations. It is a curious fact that the optical characters of these salts should be so similar, when there is so little relation chemically between magnesium, on the one hand, and yttrium and erbium on the other.

(d) Certain regularities may be observed in the spectra of the fluorescence exhibited by platino-cyanides of metals of the same family.

(e) The failure of uranyl platino-cyanide to respond to the stimulus of ultra-violet light or radium radiations is very remarkable. Both the uranyl and the platino-cyanide groups usually confer the property of fluorescence upon salts containing them. Yet when they both occur in the same compound, the latter appears to be absolutely non-fluorescent.

The suggestion has been put forth that the fluorescence "may be due to the production under the influence of ultra-violet light, the energetic ionising action of which is well known, of slight atomic electric discharges." Experiments were therefore made to determine if a crystal of platino-cyanide became electrically charged when fluorescing under the action of ultra-violet light. The results so far obtained are negative.

The foregoing account of the experiments performed is sufficient to prove that the fluorescence exhibited by platino-cyanides is no simple phenomenon. Many diverse conditions affect the character of the light emitted. The character of the basic radicle, the mode of preparation of the salt, the state of hydration, and the perfection of crystalline form, all exert their separate influences.

The author desires to express his gratitude to Dr. Fenton for valuable advice.

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CXLI.—*The Reduction of Aromatic Nitro-compounds to Azoxy-derivatives in Acid Solution.*

By BERNHARD FLÜRSCHHEIM and THEODOR SIMON.

ACCORDING to Haber's rule, nitroso- and hydroxylamino-derivatives are successively formed when aromatic nitro-compounds are reduced to amines, whilst azo-derivatives owe their formation to a condensation of the nitroso- and hydroxylamino-stages.

It has been generally accepted that this condensation during a process of reduction was only possible in neutral or alkaline solution. Goldschmidt and Ingebrechtsen (*Zeitsch. physikal. Chem.*, 1904, 48, 435) and Goldschmidt and Sunde (*ibid.*, 1906, 56, 1) even asserted that in acid solutions nitroso-compounds are further reduced with infinite velocity, which would theoretically preclude the possibility of a condensation, for Bamberger and Rising (*Annalen*, 1901, 316, 257) have shown that the latter only proceeds at a measurable rate.

Goldschmidt and Eckardt (*Zeitsch. physikal. Chem.*, 1906, 56, 385) also suppose nitroso-compounds to be reduced with infinite velocity by stannous oxide in alkaline solution; that notwithstanding this assumption azoxy-compounds were obtained, was attributed by these authors to an oxidation of the hydroxylamino-derivative by the alkali.

Recently, however, one of the authors has shown (Flürscheim, *J. pr. Chem.*, 1901, [ii], 71, 497) that in numerous cases reduction may give rise to azoxy-derivatives even in presence of strong mineral acids. Whilst Haber's rule has received further confirmation by these experiments, all the other conclusions and generalisations mentioned above must now be abandoned.

In the present research, new methods have been employed for a quantitative separation of the various products of reduction, and some of the *m*-nitro-compounds already examined were again investigated by the new methods, the research being extended to *o*-nitro-compounds, the behaviour of which is complicated by steric hindrance.

General Deductions.

The chief law established by the present investigation may be stated thus:

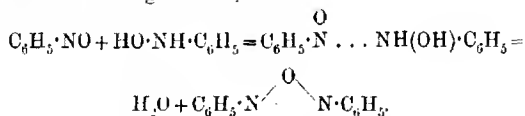
Both condensation and reduction of the intermediate products of reduction (nitroso- and hydroxylamino-derivatives) proceed at a measurable rate whether the solution be acid, neutral, or alkaline.

A priori, therefore, neither reduction of the intermediate compounds to the amine nor their condensation to azoxy-derivatives is ever excluded. The velocity of reduction and that of condensation can, however, be varied within wide limits, so that both these reactions may simultaneously take place to a variable extent, or one may be so greatly retarded as to make the other reaction appear to be the sole one.

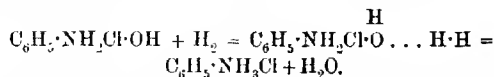
Now if the primary cause of either reaction can be established, it must be possible to foresee the conditions that will favour or delay it, and experimental confirmation of the relative rates of both reactions thus deduced has proved that this primary cause is the degree of saturation of the nitrogen atom in the hydroxylamino-compound.

Tervalent nitrogen in a hydroxylamino-compound induces condensation; quinquivalent nitrogen is incapable of condensation.

The residual affinity of the nitrogen being the cause of condensation, the reaction must be formulated with intermediate molecular addition by means of the nitrogen atoms, thus:



On the other hand, in arylhydroxylamino-salts the oxygen atom possesses considerably more residual affinity than it does in the free base, for in the latter the residual affinity of the nitrogen neutralises that of the oxygen, whereas in the salts there is no residual affinity of the nitrogen that could do so. Therefore hydrogen can unite more easily with the oxygen in the salt than in the base, and reduction follows, thus:



If, therefore, condensation is to be favoured at the expense of reduction, the proportion of free hydroxylamino-base to hydroxyl-

amino-salt in solution must be increased. This proportion again will depend on the following factors, namely :

(1) *The Strength of the Hydroxylamino-base*.—This can be varied by introducing more or less negative radicles into the benzene nucleus, whereby dissociation (hydrolysis) of the hydroxylamine in acid solution must be correspondingly augmented. If the substituents are sufficiently negative, it is possible to have practically only the free base (tervalent nitrogen) present even in an excess of strong mineral acid.

(2) *The Strength and Concentration of the Acid*.—Formation of tervalent nitrogen by hydrolysis will, of course, be the less in evidence the stronger the acid or the greater its concentration. Hydrolysis is, of course, greater in presence of acetic acid than with an equimolecular amount of hydrochloric acid.

(3) *The Nature of the Solvent*.—A dissociating solvent like water must produce a higher degree of hydrolysis than an associating solvent.

But apart from the degree of saturation of the nitrogen, there are some other influences which have to be reckoned with. One is the rate at which the reduction proceeds; this, as shown, depends on the degree of saturation of the nitrogen, but also on two other factors, namely :

(4) *the relative concentrations of nitro-compound and reducing agent,*
and

(5) *the strength of the reducing agent.*

It is evident that each molecule will be reduced more quickly if the reducing agent is dissolved in considerable quantity than where the reducing agent is gradually added. The quicker the reduction proceeds the less is the chance of condensation. If, therefore, the latter is to be favoured in acid solution, the nitro-compound must be dissolved and the reducing agent must only be added gradually. When, for instance, 1-chloro-2:4-dinitrobenzene in alcoholic hydrogen chloride is treated drop by drop with stannous chloride, the azoxy-derivative is largely formed. When, however, chlorodinitrobenzene is treated with stannous chloride and aqueous hydrochloric acid, in which it is almost insoluble, then the reducing agent will always, in the solution, be greatly in excess of the nitro-compound, and no azoxy-derivative, but only chlorophenylenediamine, is produced.

Also, a more energetic reducing agent, like zinc and hydrochloric acid, reduces, *ceteris paribus*, more quickly than a less energetic one, like tin and hydrochloric acid.

Another point which greatly affects the relative rate of reduction and condensation is

(6) *the constitution of the nitro-compound*.—Ortho-substituents may

influence the reaction owing to steric hindrance; they may also, in common with para-substituents, cause a different reaction owing to isomeric change, as will be seen later.

A glance at the tabulated experimental results of the present work, and at their graphical representation, shows the effect of the first five factors on the relative rate of reduction and condensation. It is seen that with increasing quantities of acid the yield of azoxy-compounds falls (factors 2 and 5). It might be objected that not the absolute quantity of the acid, but its concentration, should be plotted (compare Goldschmidt and Sunde, *Zeitsch. physikal. Chem.*, 1906, **56**, 1), and, in order to obviate the above objection, experiments (Nos. 5, 6, 7, 8, 9, 10) were carried out quite similarly and with the same amounts of acid, but with widely different quantities of the solvent (alcohol), and identical results were obtained in each case. If, however, 50 per cent. alcohol is used instead of absolute alcohol, the percentage of condensation rises slightly, owing to increased hydrolysis (compare factor 3).

It is further seen that stannous chloride yields more azoxy-compound when sodium acetate is added, that is, when the hydroxylamine can no longer be neutralised owing to partial hydrolysis of the stannic compounds, but only by the weaker acetic acid.

If stannous chloride is added suddenly, the proportion of condensation to reduction falls (compare factor 4, and reductions Nos. 19, 20, 23, 41, 42, 43).

The great influence of negative substituents in the nucleus (compare factor 1) is seen from the following comparison. Nitrobenzene does not yield any perceptible amount of azoxybenzene on reduction by stannous chloride even in the absence of acid, the small quantity of acid formed by partial hydrolysis of the stannous chloride being sufficient to saturate the hydroxylamino-base * (Flürscheim, *loc. cit.*).

p-Nitrobenzaldehyde, with its moderately-negative aldehydic group, yields an appreciable quantity of the azoxy-compound under the same conditions.

3:5-Dichloro-4-bromonitrobenzene and *m*-dinitrobenzene, being still more negatively substituted, in identical circumstances give an almost quantitative yield of the azoxy-compound.

Whereas all these influences (1 to 5) are simple enough, matters become less so when we proceed to consider the influence exercised by the constitution of the nitro compound (compare factor 6).

* Professor Bamberger, on being acquainted with this work, informed us that in an experiment carried out eighteen years ago, but not published, he isolated, besides aniline, some azoxybenzene on reducing nitrobenzene with tin and hydrochloric acid.

In the previous paper, the reduction of *m*-nitrobenzenesulphonic acid has shown how intramolecular salt-formation may influence the course of the reaction. In what way ortho-substituents and isomeric change may do so, now remains to be discussed.

Bamberger and Rising (*loc. cit.*) have proved that ortho-substituents, by steric hindrance, diminish the rate of condensation between hydroxylamino- and nitroso-compounds. On the other hand, it must not be overlooked that ortho-substituents also exercise a steric hindrance on most other reactions, and therefore also on the further reduction of the nitroso- and hydroxylamino-derivatives. Elbs, for instance, found that 5-nitro-8-methylquinoline is reduced to the azo-derivative by alkaline reduction, using a nickel cathode, whereas 5-nitro-6-methylquinoline, under similar conditions, only yields the amine (*Zeitsch. Elektrochem.*, 1904, 10, 579).

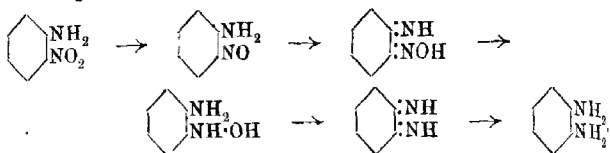
By sterically hindering both reduction and condensation, ortho-substituents therefore exercise simultaneously two opposite influences. Which of these predominates, depends on the nature of the ortho-substituent, that is, mainly on the direction in which it influences the strength of the hydroxylamino-base (compare factor 1). Thus introduction of an ortho-halogen atom in *m*-nitrophenylhydroxylamine diminishes its basic properties very considerably, whereas the latter are increased when a methyl group is in the same position. That this is the case may be deduced from numerous facts; for example, *o*-chloronitroaniline is a much weaker base than *m*-nitroaniline, and nitrotoluic acids are much weaker acids than the corresponding nitrobenzoic acids (van Scherpenzeel, *Rec. trav. chim.*, 1901, 20, 149).

Consequently, hydrochloric acid counteracts hydrolysis more in the case of the hydroxylamino-compound derived from dinitrotoluene than in that of the corresponding compound derived from dinitrobenzene, and less in the case of the hydroxylamino-compound derived from chlorodinitrobenzene or bromodinitrobenzene.

As to isomeric change during reduction, an instance is furnished by dinitrodiphenylamine. This compound might be expected to behave like dinitrotoluene or bromodinitrobenzene; it yields, however, exclusively the amine.

Further, Elbs has shown that alkaline electro-reduction of *o*- and *p*-nitroaniline and nitrophenols furnishes amines only. Similar observations were made by Bamberger (*Ber.*, 1895, 28, 250) with a neutral solution (zinc dust and water). H. Goldschmidt and Eckardt (*loc. cit.*) likewise observed that alkaline stannous oxide transforms *o*- and *p*-nitroaniline into the amino only, and explained this by the erroneous assumption that the nitroso-compound is reduced at an infinite rate.

A very plausible explanation, however, has been put forward by Elbs (*Zeitsch. Elektrochem.*, 1901, 7, 134), and is shown by the following scheme:



The present observations may be taken to prove that these intramolecular changes occur in an acid solution as well, and that either one or both of them must proceed at a very high rate. A different explanation, based on the partial saturation of the hydroxylamino-nitrogen through the influence of unsaturated nitrogen or oxygen in the ortho-position (compare Flürscheim, *J. pr. Chem.*, 1907, [ii], 76, 185, and previous papers), is, however, by no means excluded, and experiments which are in progress with o-nitroamines containing a tertiary amino-group may decide this point.

Graphical Interpretation of Results.

By plotting the amount of acid used against the yield, curves may be obtained. The ordinates may represent: (a) the amount condensed (C) in proportion to the total amount condensed and reduced (C+R), or (b) the proportion of azoxy-compound to amine (C/R), or (c and d) the ordinates A and B corrected so as to show the values C/C+R and C/R which would be obtained if the concentration of the nitro-compound remained constant during reduction.

Only the ordinates C and D being comparable, it is necessary to show how they may be arrived at.

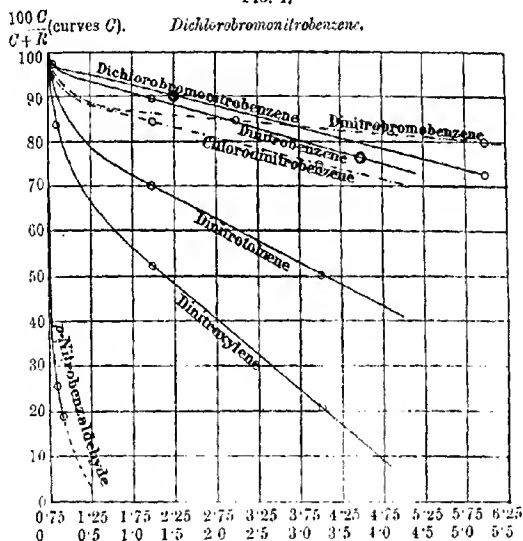
For the nitroso- and hydroxylamino-compounds, a stationary equilibrium is established during the progress of a reduction; the concentration representing this equilibrium gradually changes along with the gradual disappearance of the nitro-compound.

It will be shown below that for a given compound and a given volume of solution, the average rate of reduction is almost exclusively a function of the rate at which stannous chloride is added; that, on the other hand, the rate of condensation is proportional to the product of the concentrations of nitroso-compound and hydroxylamine, which vary (other circumstances being equal) in proportion to the nitro-compound. In order to obtain the ordinates D, the ordinates B must therefore be multiplied by the square of the initial concentration of the nitro-compound and divided by the average of the squares of all subsequent concentrations. Instead of the latter, the square of the

arithmetical means of initial and final concentrations may be substituted approximately. As the volumes disappear on division (the change of dilution caused by the gradual adding of the solvent of the stannous chloride having, as will be seen, no influence), it is possible to use the absolute amounts of the nitro-compound present before and after reduction, the latter being obtained by deducting the highest yield of reduction products from the initial amount.

The curves C, obtained from D, were found to be mainly straight lines, and served to calculate intermediate points of curves D.

FIG. 1.



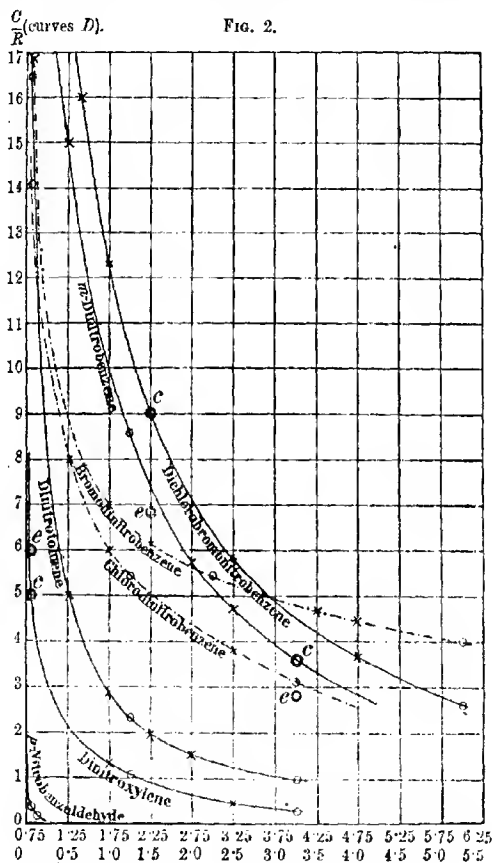
The upper figures for the abscissae represent the amount of acid (in grams) added before reduction; the lower figures the average amount actually present during reduction (see text). The acid is calculated per 4 grams of dinitrobenzene and equimolecular amounts of the other nitro-compounds.

In curves C and D, the ordinates marked by circles correspond with experiments (see tables); those marked by crosses, in curves D, have been obtained from the straight sections of curves C.

The values for those reductions, where the standard time of 20 minutes for adding the stannous chloride had not been observed (marked with two asterisks in tables), were, for the full curves, reduced to 20 minutes by calculation, and the mode of calculation was checked by experiment (compare reductions of dinitrotoluene with 4 grams of acid, which were carried out in 15 and in 20 minutes). In curves D, these corrected values are shown by two circles and a \times , the original values by two circles and an \circ . In curves C, only the corrected values are given, and they are also shown by two circles.

By applying the law of hydrolysis deduced below, it can be shown that the ordinates D must stand to their abscissae in the relation of

inverse geometrical progressions. For the ratio, 2, of the progression of the abscissæ, $1/1.8$ becomes the approximate ratio of the ordinates. Considering the high concentrations and the difficulty of adding the stannous chloride at an exactly uniform rate, the diagrams show a very satisfactory agreement with this postulate. Only chloro- and



bromodinitrobenzene are less influenced by the acid than would correspond with the factor $1/1.8$. This means that the proportion, hydroxylamino-base to salt, does not fall with increase of acid to the extent required by the law of hydrolysis, but less than this. The explanation is that the free base is primarily formed by reduction, and

that the rate at which it combines with acid is proportional to its basic strength and inversely proportional to the steric hindrance; the first being here small and the latter pronounced, the hydrolytic equilibrium which is disturbed by reduction of the salt cannot be restored with sufficient velocity.

This effect of an ortho-substituted halogen and the absence of such an influence in the case of an ortho-substituted methyl group are confirmed by the velocity coefficients for addition of allyl bromide [compare Menshutkin, (van't Hoff, *Vorlesungen*, 2, 94)], which are :

	K.
Aniline	68
<i>o</i> -Toluidine	54
<i>o</i> -Chloroaniline	9

The top figures in the diagrams simply represent the amount of acid added before reduction. The actual amount present during the reduction might, however, be different: (a) on account of hydrolysis of stannous chloride; (b) by hydrochloric acid being used to transform stannous into stannic chloride, which may again be hydrolysed or may associate itself with more hydrochloric acid, and (c) by neutralisation of some hydrochloric acid by the amines formed during reduction.

As to (a), whenever stannous chloride is added drop by drop, it is not present in sufficient amount to allow its inconsiderable hydrolysis to have any appreciable effect.

With regard to (b), alcoholysis of stannic chloride always produces the same stable compound, $\text{SnCl}_2(\text{OR})_2\text{HCl}$, where R may be methyl, ethyl, phenyl, or salicyl (Rosenheim and Schnabel, *Ber.*, 1905, 38, 2777). Alcoholic oxidation undoubtedly leads to the same compound, containing per molecule one molecule of hydrogen chloride more than stannous chloride, and therefore diminishing the free acid to that extent as is expressed by the lower figures in the diagrams. This is experimentally confirmed by the fact that the result of the reduction is independent of concentration, and that the progression of the curves agrees with the theory. If, instead of always producing the same compound, $\text{SnCl}_2(\text{OEt})_2\text{HCl}$, the degree of alcoholysis were variable, this would obviously be impossible.

(c) The amine formed can undoubtedly neutralise part of the acid, and its hydrochloride may form a double salt with stannic chloride, thereby protecting the latter from hydrolysis. But *p*-nitrobenzaldehyde is the only compound the curve of which required correcting on that account (when it lay a little below its original position); in all the other cases, the amount of acid neutralised by the amine is insignificant relative to the total amount of acid present. This applies equally to the amount of tin double salt formed by the amine

hydrochloride, especially as such double salts need not be compounds of stannic tetrachloride, but may be derived from the oxychloride or its ethoxylated analogue (as, for example, the double salt of stannic oxychloride with the ester of dimethylphenolphthalein, which was recently obtained, notwithstanding the presence of an excess of acid, by Green and King, *Ber.*, 1907, 40, 3732).

Kinetics of the Reduction.

Taking the case of two reductions carried on within the same time, and calling the respective concentrations, at any given time, of the nitro-compound γ_n and γ_{1n} , of the acid γ_a and γ_{1a} , stannous chloride γ_s and γ_{1s} , nitroso-compound γ_i and γ_{1i} , hydroxylamine-base γ_H and γ_{1H} , and of the hydroxylamine-salt γ_{Hs} and γ_{1Hs} the stationary state for the hydroxylamine is represented by the equations:

$$\frac{d\gamma_{Hs}}{dt} + \frac{d\gamma_H}{dt} = \frac{d\gamma_i(\text{Reduction})}{dt}$$

and

$$\frac{d\gamma_{1Hs}}{dt} + \frac{d\gamma_{1H}}{dt} = \frac{d\gamma_{1i}(\text{Reduction})}{dt}.$$

These changes of concentration being proportional to the concentrations themselves, we get:

$$(1) \quad \frac{d\gamma_H}{d\gamma_{Hs}} = \frac{d\gamma_i - d\gamma_{Hs}}{d\gamma_{Hs}} = \frac{K_1 \times \gamma_i \times \gamma_s \times F\gamma_s - K_2 \times \gamma_{Hs} \times \gamma_s \times F\gamma_s}{K_2 \times \gamma_{Hs} \times \gamma_s \times F\gamma_s} = \frac{K_1}{K_2} \times \frac{\gamma_i}{\gamma_{Hs}} - 1$$

and

$$(1a) \quad \frac{d\gamma_{1H}}{d\gamma_{1Hs}} = \frac{K_1}{K_2} \times \frac{\gamma_{1i}}{\gamma_{1Hs}} - 1,$$

where K_1 and K_2 are constants and $F\gamma_s$ and $F\gamma_{1s}$ express a possible influence of the concentration of the acid on the rate of reduction.

In this case, all the concentrations may vary in a different degree. If the dilution varies q -fold, we have $\gamma_{1n} = q \times \gamma_n$; $\gamma_{1i} = q \times \gamma_i$.

If, moreover, stannous chloride is added in both cases at the same rate, it is an experimental fact (see above) that the proportion, condensation/reduction, remains constant. Since this applies equally to corresponding small intervals in both reductions, it follows that

$$\frac{d\gamma_{1n}}{dt} = \frac{d\gamma_n(\text{Cond.})}{dt} + \frac{d\gamma_{1i}}{dt}(\text{Reduction}) = r \times \frac{d\gamma_n(\text{Cond.})}{dt} + r \times \frac{d\gamma_i}{dt}(\text{Reduction})$$

and

$$\frac{d\gamma_n}{dt} = \frac{d\gamma_n(\text{Cond.})}{dt} + \frac{d\gamma_i}{dt}(\text{Reduction}),$$

where r is a coefficient expressing the change both of rate of reduction and condensation of the nitroso-compound.

Therefore

$$(2) \quad \frac{d\gamma_{1a}}{d\gamma_a} = \frac{K_3 \times \gamma_{1a} \times F\gamma_{1a} \times \gamma_{1t}}{K_3 \times \gamma_a \times F\gamma_a \times \gamma_t} = r$$

and

$$(3) \quad \frac{d\gamma_{1a}}{d\gamma_{1a}} = \frac{K_2 \times \gamma_{1a} \times F\gamma_{1a} \times \gamma_{1t}}{K_2 \times \gamma_{1a} \times F\gamma_a \times \gamma_t} = r, \text{ and } \frac{d\gamma_{1a}}{d\gamma_{1a}} = \frac{K_4 \times \gamma_{1a} \times \gamma_{1t}}{K_4 \times \gamma_{1a} \times \gamma_{1t}} = r.$$

By combining 2 and 3 :

$$(4) \quad \frac{\gamma_{1a}}{\gamma_a} = \frac{\gamma_{1a}}{\gamma_{1a}} = q.$$

C/R being constant, we also have

$$(5) \quad \frac{d\gamma_{1a}}{d\gamma_{1a}} = \frac{d\gamma_{1a}}{d\gamma_{1a}},$$

or, from 1 and 1a,

$$\frac{\gamma_{1t}}{\gamma_{1a}} = \frac{\gamma_{1t}}{\gamma_{1a}},$$

or

$$(6) \quad \frac{\gamma_{1t}}{\gamma_t} = \frac{\gamma_{1a}}{\gamma_{1a}} = q.$$

From (3) we obtain

$$(7) \quad \frac{\gamma_{1a}}{\gamma_a} = \frac{\gamma_{1a}}{\gamma_{1a}} \times \frac{F\gamma_{1a} \times \gamma_{1t}}{F\gamma_a \times \gamma_t} \times \frac{\gamma_t}{\gamma_{1t}}.$$

The value for $\frac{F\gamma_{1a} \times \gamma_{1t}}{F\gamma_a \times \gamma_t}$ can easily be arrived at. If in both reductions stannous chloride is added drop by drop within the same time, each drop must either be oxidised at once, when the quantity contained in a drop would yield the maximum concentration of the stannous chloride, or a higher concentration of a stationary character may be reached, which is actually the case. This may be deduced from expts. 22 and 23 (see tables). In No. 22, stannous chloride was added drop by drop within twenty minutes; in No. 23, all at once. If each drop were used up as soon as added, the concentration of stannous chloride in No. 23 would exceed that in No. 22 several hundred times, and the yield of azoxy-compound would correspondingly have fallen to less than one per cent. As it only falls to 35.5 per cent., the average concentration of stannous chloride must be considerable. As soon as this stationary state has been reached, the rate of reduction remains constant for a constant volume. If the volume of the reacting liquid is reduced to 1 qth, the change per volume unit for corresponding intervals, and therefore also on the average of the whole reaction, must rise q -fold; since the same applies to the concentration of the nitro-compound, we have for its rate of

change (and similar considerations apply to the nitroso-compound and the hydroxylamino-salt):

$$\frac{d\gamma_{1u}}{d\gamma_u} = \frac{K_2 \times \gamma_{1u} \times \gamma_{1s} \times F\gamma_{1a}}{K_3 \times \gamma_u \times \gamma_s \times F\gamma_a} = \frac{K_2 \times q \times \gamma_u \times \gamma_{1s} \times F\gamma_{1a}}{K_3 \times \gamma_u \times \gamma_s \times F\gamma_a} = q.$$

or

$$(8) \quad \frac{\gamma_{1s} \times F\gamma_{1a}}{\gamma_s \times F\gamma_a} = 1.$$

From (6), (7), and (8) we get: (9) $\gamma_{1u} = \gamma_u$, and from (3), (4), and (9): $r = q$.

By combining the equations $\frac{\gamma_{1u}}{\gamma_{1s}} = q$; $\frac{\gamma_{1a}}{\gamma_a} = q$, and $\gamma_{1u} = \gamma_u$,

we get

$$\frac{\gamma_{1u} \times \gamma_{1a}}{\gamma_{1s}} = \frac{\gamma_u \times \gamma_a}{\gamma_{1s}} = K,$$

or

$$\frac{\text{base} \times \text{acid}}{\text{salt}} = \text{constant}.$$

Therefore this fundamental equation for the hydrolysis of salts of a weak base with a strong acid, or vice versa, equally applies to alcoholic solutions (for hydrochloric acid). In view of the known behaviour of strong electrolytes in alcoholic solutions, this result could not a priori be foreseen.

A word may be said on the influence which steric hindrance exercises on the average concentration of stannous chloride during reduction. It lowers the constants K_1 , K_2 , K_3 , and K_4 ; the rate of adding stannous chloride remaining unchanged, its concentration must rise to reach a stationary equilibrium. Therefore, for instance, the average concentration of stannous chloride must be greater for bromodinitrobenzene than for dinitrotoluene. If, then, stannous chloride be added, on the one hand, all at once, thus giving an average concentration of half the amount added, and, on the other, by drops, the values for C/R must be more affected for dinitrotoluene than for bromodinitrobenzene. This is actually so (compare reductions 41, 42, and 43 with 45 and 46, and 19 and 20 with 17 and 18), C/R being reduced by one-half for bromodinitrobenzene and by two-thirds for dinitrotoluene.

These kinetical considerations also give a quantitative explanation for factors 4 and 5 under "General Deductions." If the nitro-compound¹ is sparingly soluble, γ_u , γ_{1u} , and γ_s all become very small; if this retards reduction by a certain factor, it must—the concentration of the reducing agent being kept unchanged—retard condensation by the square of that factor.

If a reducing agent is replaced by one of greater strength, the constants K_1 to K_3 become greater, whereas K_4 remains unchanged.

EXPERIMENTAL.

Methods.—The reductions were carried out on a water-bath in a flask connected with a reflux condenser and fitted with a dropping funnel, the exact conditions for each experiment being described in the tables. By titration before and after reduction, it was ascertained that no hydrogen chloride escaped through the condenser.

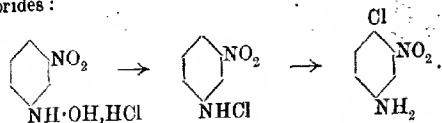
The tin was always precipitated by sodium hydrogen carbonate. The solution was heated, sufficient solvent added to redissolve any precipitate, and then carefully neutralised by powdered sodium hydrogen carbonate. The warm solution was filtered and, where the amine was not volatile with alcohol, evaporated, the residue dissolved in benzene, and the amines precipitated by dry hydrogen chloride. In the case of dichlorobromonitrobenzene, the amine was volatile and the azoxy-compound insoluble; the latter was therefore collected after some time, the tin removed as above, and the filtrate shaken with dry sodium sulphate, acidified, and evaporated. The residue was boiled with benzene, treated with hydrogen chloride, and filtered. Traces of inorganic matter in the amine were determined by incineration of a portion.

In all cases the precipitated tin retained some organic matter, which was removed by drying and pulverising the precipitate, extracting with ethyl acetate, and evaporating the latter and adding it to the main portion. Where an aminopheuol was formed, the greater part remained as the sodium derivative.

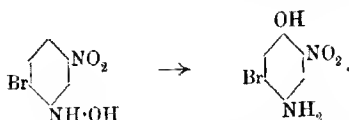
The benzene solution containing the nitro- and azoxy-compounds was distilled in steam until only the azoxy-compound remained. In no case was the latter volatile, but it sometimes formed resinous lumps which partly retained the nitro-compound, so that it had to be re-dissolved in acetone and again distilled. Finally, a solid mass was always obtained entirely free from nitro-compound.

The precipitated amine hydrochlorides were dried for twenty-four hours at the ordinary temperature and weighed. When obtained from dinitro-compounds they contained, in addition to some diamine, amino-derivatives of the azoxy-compound, formed by secondary reduction of the nitroazoxy-compounds (compare Flürscheim, *loc. cit.*). Moreover, small amounts of nitroazoxy-compounds were often precipitated along with the amines. Sometimes (for instance, in reductions Nos. 5, 7, 8, 19, 20, but never with dinitroxylyene, where both para-positions are occupied) the hydrochlorides of chloro-amines were present,

produced by intramolecular rearrangement of the hydroxylamine hydrochlorides:



Lastly (for instance, in Nos. 2, 5, and especially in all reductions with chloro- and bromo-dinitrobenzene, but never with dinitroxylene), there were some aminophenol hydrochlorides, also formed by rearrangement:



To separate all this, the precipitate was dissolved in alcohol, neutralised with sodium acetate, and distilled in steam. The amines and halogen-substituted amines passed over, whereas the nitroazoxy-compounds, aminoazoxy-compounds, and aminophenols remained in the flask, the latter as salts forming a red solution, from which, after acidification, they were extracted with ethyl acetate, and the former two separating as solids. The termination of the distillation, which usually lasted a day or two, was indicated by the distillate, at first yellow, finally becoming colourless. The weight of the distillate was obtained by difference.

For *p*-nitrobenzaldehyde and 2:4-dinitrodiphenylamine, different methods were employed.

The accuracy of the percentage figures is within about ± 2 per cent., which figure the total experimental error should not exceed.

Tabular Summary of Reductions.

The percentage figures were arrived at in the following way:

$$100 \times \text{condensation} \cdot (\text{condensation} + \text{reduction}) = 100 \times C/C + R =$$

$$\frac{\text{azoxy-} + \text{aminoazoxy-compounds}}{\text{azoxy-} + \text{aminoazoxy-compounds} + \text{amino} + \text{diamine} + \text{halogen-amine}}$$

the equivalent amount of the corresponding nitro-compound being taken for each substance instead of the quantity actually determined.

The diamine, being formed by the secondary reduction of the amine, is included in its weight without separation, the second molecule of hydrogen chloride which it contains counterbalancing its smaller molecular weight. The chloro-amine was proved to be present in traces only, and could be neglected. The weight of the amino-

phenol (which is not derived from the hydroxylamine either by reduction or condensation) was merely estimated in order to subtract it from the weight of the amine which it accompanied.

No.	HCl-gas (grams).		Alcohol (c.c.).		Time of adding SnCl ₂ (mins.).	Sodium acetate with nitro-com- pound (grams).	Yield of (in grams)			
	With SnCl ₂	With nitro- compound.	With SnCl ₂	With nitro- compound.			Amine hydro- chloride.	Azoxyamine.	Azoxy-com- pound.	$\frac{100C}{C+R}$ (ordinates A).
<i>m</i> -Dinitrobenzene : 4 grams.										
1	0	0	30	55	40	12	0.00	0.00	1.6	100
2	0	0	30	55	40	12	0.00	0.00	1.5	100
3	0	0	30	30	30	0	0.06	0.1	1.95	97.5
4	0	0	30	30	20	0	0.1	0.15	2.1	96.5
5	0	2	35	165	20	0	0.19	0.15	1.6	80.5
6	0	2	35	42+30 water	20	0	0.35	0.11	1.7	86.0
7	0	2	35	40+30 water	12	0	0.34	0.09	1.65	85.5
8	0	2	35	40	20	0	0.4	0.19	1.4	82
9	0	2	35	42	20	0	0.41	0.17	1.33	81
10	0	2	40	167	20	0	0.52	0.15	1.5	79
11	0	4	30	65	15	0	0.77	0.2	0.84	61.5
12	8	0	86	30	27	0	0.8	0.15	0.75	57
13	8	0	51	30	20	0	0.94	0.17	0.68	52
14	12	0	60	30	30	0	0.94	0.14	0.64	50

2:4-Dinitrotoluene : 4.35 grams.

15	0	0	30	60	20	12	0.06	0.25	2.1	93
16	0	0	30	30	35	0	0.3	0.15	1.9	89
17	0	0	30	30	20	0	0.29	0.14	1.85	89
18	0	0	30	30	15	0	0.23	0.11	1.76	90
19	0	0	30	30	at once	0	0.81	0.19	1.72	73
20	0	0	30	30	at once	0	0.8	0.12	1.64	72
21	1	0	38	30	20	0	0.5	0.14	1.66	81
22	0	2	30	37	20	0	1.15	0.15	1.03	54.5
23	0	2	30	42	at once	0	1.28	0.1	0.5	35.5
24	4	0	61	30	30	0	1.1		1.05	—
25	0	4	30	54	20	0	1.46	0.12	0.55	35
26	0	4	30	60	15	0	1.33	0.1	0.4	27.5
27	0	4	30	60	15	0	1.58	0.1	0.4	27
28	8	0	60	30	20	0	1.44	0.10	0.40	35.5

4:6-Dinitro-*m*-xylene : 4.65 grams.

29	0	0	30	60	12	12	0.04	0.06	2.42	98.5
30	0	0	40	40	25	0	0.67	0.15	1.56	74.5
31	0	2	30	42	20	0	0.96	0.1	0.51	42
32	0	4	30	64	20	0	1.38	0.02	0.16	15

No.	HCl-gas (grams).		Alcohol (c.c.).		Time of adding SnCl ₂ (mins.).	Sodium acetate with nitro-com- pound (grams).	Yield of (in grams).			100 C C+R (ordinates A).
	With SnCl ₂	With nitro- compound.	With SnCl ₂	With nitro- compound.			Amine hydro- chloride.	Azoxyamine.	Azoxy-com- pound.	
1-Chloro-2 : 4-dinitrobenzene : 4.8 grams (in No. 39, 9.6 grams).										
*33	0	0	30	30	20	0	0.31	0.11	1.85	88
*34	0	0	30	30	20	0	0.36	0.13	2.15	88
35	1	0	62	30	20	0	0.67		1.4	—
36	4	0	62	30	20	0	0.9		1.3	—
*37	0	2	30	42	20	0	0.67	0.26	1.48	74.5
*38	0	4	30	65	12	0	1.04	0.2	1.23	61.5
39	0	8	50	98	30	0	2.65		2.9	—
1-Bromo-2 : 4-dinitrobenzene : 5.9 grams (in No. 44, 1.5 grams).										
40	0	0	60		at once	0	0.7 (including aminophenol)		—	—
41	0	0	30	30	at once	0	0.46	0.03	2.2	86
42	0	0	35	50	at once	0	0.45	0.03	2.69	87
43	0	0	30	50	at once	0	0.52	0.15	2.73	86
44	0	0	0	25	—	3	0	0	0	0
*45	0	0	30	30	30	0	0.26	0.21	2.7	92.5
*46	0	0	30	30	25	0	0.29	0.27	2.58	91.5
*47	0	3	30	58	20	0	0.86	0.2	1.97	74
*48	0	6	30	78	20	0	1.13	0.15	1.86	66.5
3 : 5-Dichloro-4-bromonitrobenzene : 6.45 grams.										
*49	0	0	35	45	20	0	0.25	0	5.05	96
50	0	0	35	50	22	0	—	0	5.07	—
*51	0	2.25	30	44	14	0	1.17	0	3.1	74.5
							(calc.)			
*52	0	6	30	78	20	0	1.74	0	2.05	56
							(calc.)			
*53	0	6	70	79	20	0	1.8	0	1.98	54.5
p-Nitrobenzaldehyde : 3.6 grams (in Nos. 55 to 58, 7.2 grams).										
54	0	0	30	60	17	12	1.3	Free base p-azoxy benzoic acid	0	0.53 39
							(calc.)			
*55	0	0	50	60	20	0	2.4		0	0.55 17
*56	0	0	50	60	20	0	2.6		0	0.53 16.5
*57	0	0	50	60	20	0	2.3		0	0.58 17.5
							(calc.)			
*58	0	1	70	56	25	0	2.35		0	about 12
							(calc.)			
2 : 4-Dinitrodiphenylamine : 6.15 grams (in No. 59, 2.05 grams).										
59	0	0	12	50	20	0	0.9	0	0	0
60	0	0	25	30	20	0	—	0	0	0

In all experiments, the amount of stannous chloride corresponded in reducing power with 7.2 grams of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$; the reducing strength of the stannous preparations varied between 80 per cent. and 95 per cent. of that of the pure compound. Only in Nos. 39, 55, 56, 57, and 58 was double the above amount used; in No. 59, one-third, and in No. 44, none.

Where stannous chloride was added all at once, the solution was immediately boiled for some time.

The experiments used for the diagrams are marked with one or two asterisks, according as the time of reduction was twenty minutes or not.

For *p*-nitrobenzaldehyde and dichlorobromonitrobenzene, the amount of amine compound could be calculated from the amounts of azoxy-compound obtained and stannous chloride used, no secondary reactions occurring in these cases.

Observations Concerning Some of the Reductions.

The azoxy-amines, probably with an admixture of azo-amines, were invariably brown, almost insoluble in water, and soluble in acids with a brown colour, which became paler on adding sodium nitrite.

Dinitrobenzene and Dinitrotoluene.—In some cases (for example, Nos. 2, 5, 8, 15, 19, 20) a soluble, non-basic product was formed, which was contained in the filtrate from the azoxy-compound after distillation. It gave an intense violet coloration with ammonia. The derivative from dinitrobenzene was obtained as a brown solid on extracting its acid solution with ethyl acetate; the corresponding dinitrotoluene derivative was obtained as a dark precipitate on adding an acid to its violet solution in ammonia. *p*-Benzoquinone derivatives, especially *p*-benzoquinoneoxime, are known to be amongst the decomposition products of arylhydroxylamines, and the violet solution of *p*-aminophenol in alkalis is ascribed to the formation of similar compounds. In this connexion, a characteristic reaction for *m*-dinitrobenzene was discovered. A trace is dissolved in boiling water, and, on adding some drops of aqueous sodium hydroxide and a trace of an aqueous solution of stannous chloride, an intense violet colour is produced. This reaction is still quite distinct in a concentration of dinitrobenzene of 1 to 10,000. Other nitro-compounds behave differently. Dinitrotoluene gives a yellow, nitrobenzene a pale yellow, coloration, whereas 1:3:5-trinitrobenzene shows an intense red colour with alkali alone.

The azoxy-compound obtained from dinitrotoluene was never perfectly homogeneous. A comparatively pure product melting at about 140° was obtained in expt. 22, whilst Woyprecht (*Diss.*, Giessen,

1902) gives 144—147°. In some cases the conditions precluded the formation of a polyazoxy-compound (compare Flürscheim, *loc. cit.*); it must therefore be assumed that the para-nitro-group is also attacked to a small extent, giving rise to the formation of an isomeric azoxy-compound.

Dinitroxylene.—Commercial dinitroxylene (Schuchardt) is a mixture of 4:6-dinitro- and 2:4-dinitro-*m*-xylene, which is best separated by acetic acid. A few experiments were made with the commercial mixture, which invariably yielded less of the azoxy-compound and more amine than did the pure 4:6-dinitro-*m*-xylene. This is, of course, due to the presence of the isomeride, one nitro-group of which, being placed between two methyl groups, is practically incapable of condensation (compare Bamberger and Rising, *loc. cit.*). It is therefore this nitro-group which is first attacked.

The dinitroazoxyxylene from expt. 31, after two crystallisations from acetic acid, melted and decomposed at 185—190°, and gave the following results on analysis:

0.0744 gave 10.9 c.c. N_2 (moist) at 21° and 758 mm. $N = 16.6$.

$C_{16}H_{16}O_5N_4$ requires $N = 16.3$ per cent.

Chlorodinitrobenzene.—In confirmation of previous observations, it was found that the *o*-nitro-group is almost exclusively reduced, since the amine (No. 36), after separation from diamine and azoxy-amine, at once crystallises from water and melts at 110—115°, instead of 116—117°, whereas the isomeric 4-chloro-5-nitroaniline melts at 102—103°. Similarly, the crude acetyl derivative obtained from the amine melted at 145°, instead of 153—154°, the isomeride melting at 99—100°.

The azoxy-product (No. 36) when crystallised from concentrated nitric acid was found to be a mixture melting at 120—160°.

Bromodinitrobenzene.—That also here practically only the *o*-nitro-group was attacked could be shown in expt. 45, where the amine obtained from the steam distillate, when precipitated by ammonia from its solution in dilute hydrochloric acid, melted at 139°, the melting point of pure 2-bromo-5-nitroaniline being 139—140°.

The azoxy-compound obtained by a reduction not given in the tables, where for 3.95 grams of bromodinitrobenzene 4 grams of hydrochloric acid were added to the stannous chloride, gave the following result on analysis:

0.1805 gave 20.2 c.c. N_2 (moist) at 18° and 769 mm. $N = 13.1$.

$C_{12}H_6O_5N_3Br_2$ requires $N = 12.6$ per cent.

The difference is due to an admixture of polyazoxy-compounds (compare Flürscheim, *loc. cit.*).

Expts. 40 and 41 served finally to decide the question; at what stage

bromine is eliminated when bromodinitrobenzene is reduced to *m*-phenylenediamine by tin and hydrochloric acid (C. L. Jackson, *Amer. Chem. J.*, 1896, **18**, 466; Blanksma, *Rec. trav. chim.*, 1905, **24**, 320). Both these authors rightly supposed that bromine is only eliminated from the diamine. In support of this view, Jackson showed that bromophenylenediamine loses a bromine atom on treatment with tin and hydrochloric acid, but it might equally be removed from the dinitro-compound or from the nitroaniline. To show that such is not the case, the following experiments were carried out, which prove that if complete reduction by tin and acid in aqueous solution is replaced by partial reduction by stannous chloride and acid in alcohol, no bromine is eliminated.

(1) If bromine were removed from the bromodinitrobenzene or from the bromonitroaniline, the latter would contain nitroaniline. Accordingly, the amino-group was eliminated, whereby minute quantities of a nitroaniline may be detected by the odour of nitrobenzene and by the hypochlorite reaction of aniline after reduction (as was specially ascertained by a corresponding test with *m*-nitroaniline). No trace of nitroaniline was present. (2) If bromine had been removed, the neutralised stannic acid mixture would contain sodium bromide. Accordingly, after careful removal of the sodium salt of aminophenol by means of acetone, the inorganic mixture was tested for bromine, which was shown to be completely absent.

It was further ascertained that very little diamine is formed during these partial reductions of bromodinitrobenzene, the amount being, in expt. 40, less than 0.05 gram.

Finally, the action of alcoholic sodium acetate on bromodinitrobenzene was examined. On boiling for forty minutes, no reduction took place, but some bromine was displaced by hydroxyl, 0.03 gram of silver bromide being obtained, whilst the yellow solution contained some dinitrophenol in the form of its sodium derivative.

The dibromodinitroazoxybenzene obtained from expt. 48 was sparingly soluble in acetic acid, and crystallised from it in dark yellow crusts melting and decomposing at 160—180°.

Dichlorobromonitrobenzene.—In the preparation of this compound (compare Flürscheim, *loc. cit.*), the proportions were somewhat altered. Twenty-two grams of 2:6-dichloro-4-nitroaniline were dissolved in 450 c.c. of glacial acetic acid, and 88 c.c. of concentrated hydrobromic acid and 33 grams of sodium nitrite were added to the hot solution. When the evolution of nitrogen had ceased, the whole was cooled and poured into a little more than the same volume of water. The crude product weighed 28 grams, that is, almost the theoretical yield, and, after a single crystallisation from alcohol, showed the correct melting-point, 88°. On reducing the amount of acetic acid by one-third and

the hydrobromic acid by one-fourth, an equal yield of an almost equally pure product was obtained.

p-Nitrobenzaldehyde.—The following compounds were obtained in varying amounts:

(1) Unchanged nitrobenzaldehyde; (2) azoxybenzaldehyde; (3) polymeric aminobenzaldehyde hydrochloride; (4) anhydro-bases, formed by the condensation of aminobenzaldehyde with nitrobenzaldehyde and azoxybenzaldehyde.

Where the amine was not determined, the azoxyaldehyde was obtained by oxidising the total organic matter with permanganate and separating the azoxybenzoic acid from the nitrobenzoic acid by methyl alcohol. To ascertain that no azoxybenzoic acid was formed by the action of permanganate on aminobenzaldehyde, just as alkaline permanganate oxidises aniline to azoxybenzene, the oxidation was repeated in most cases with chromic acid in sulphuric acid, and practically identical results were obtained.

As concentrated solutions of chromic acid carry the oxidation too far, 1 part of chromic acid in 1.8 parts of sulphuric acid and 8 parts of water was used, which on boiling for a few minutes was found to convert *p*-nitrobenzaldehyde quantitatively into the acid. Accordingly, the mixture of aldehydes was dissolved in concentrated sulphuric acid, treated with finely-powdered sodium nitrite to prevent oxidation of the amino- to the azoxy-group, and then treated with chromic acid in the above proportions.

Further, it was ascertained that the alcohol used for precipitating the excess of permanganate does not transform nitrobenzoic acid into azoxybenzoic acid by alkaline reduction.

The estimation of the amine proved rather complicated. Reduction being at an end, the cooled solution was separated from the crystalline deposit (a mixture of nitro- and azoxy-benzaldehyde) and evaporated, then treated with sodium hydrogen carbonate, and extracted with ethyl acetate. The residue from the latter was treated with benzene, when a portion remained undissolved; it consisted mostly of polymeric aminobenzaldehyde, and in addition some anhydro-bases which yielded on oxidation an amount of nitro- and azoxy-benzoic acids corresponding with the nitro- and azoxy-aldehyde parts of the anhydro-base molecules. By deducting this portion from the total weight of the substance insoluble in benzene, the amine contained in the latter was obtained.

From the benzene solution, hydrogen chloride precipitated the hydrochlorides of anhydro-bases and polymerised aminobenzaldehyde, in which azoxy- and nitro-benzaldehydes were again determined by oxidation and deducted. The benzene filtrate then only retained azoxy- and nitro-benzaldehydes.

Polymeric aminobenzaldehyde and its red hydrochloride were identified by their characteristic behaviour, as was also the azoxybenzoic acid; the latter dissolved in sodium carbonate or pyridine with a marked yellow colour, and was precipitated by acids; it was practically insoluble in ordinary solvents, and did not melt.

Dinitrodiphenylamine.—In expt. 59, 1.05 grams of the dinitrodiphenylamine were recovered on evaporation of the filtrate from the precipitated amine. By fractional crystallisation and mixed melting-point tests, it was ascertained that no trace of an azoxy-compound was present. A similar result was obtained in expt. 60.

In conclusion, the authors wish to express their acknowledgment of the facilities placed at their disposal at the Davy-Faraday Research Laboratory of the Royal Institution, where the present work has been carried out.

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ERRATA.

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ERRATA.

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PART I.

Page	Line	
336	12	} for "arylsulphonates" read "arylsulphinates."
337	20	

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PART I.

233	16	for "phenylrhodanic" read "anilinorhodanic."
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BONE AND COWARD'S PAPER.

1218	Table IX, 3rd column	for "23.90" read "3.90"
		1.40 21.40.
1219	„ X, 6th „ „	„ 71.9" read "28.1"
		23.1 71.9.
1222	„ XII for	Percentage composition of gaseous products, $\begin{pmatrix} \text{H}_2 \\ \text{C}_2\text{H}_2 \\ \text{C}_2\text{H}_4 \\ \text{C}_2\text{H}_6 \\ \text{CH}_4 \end{pmatrix}$ " read Percentage composition of gaseous products, $\begin{pmatrix} \text{C}_2\text{H}_2 \\ \text{C}_2\text{H}_4 \\ \text{C}_2\text{H}_6 \\ \text{CH}_4 \\ \text{H}_2 \end{pmatrix}$ "

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PART I.

Page	Line	
406	11*	for "1-isopropylheptane-2-one" read "1-isopropylcyclohexane-2-one."
457	20*	„ "4-nitro-4'-hydroxydiphenylamine" read "4-nitro-4'-hydroxydiphenylamine."
474	4	„ "aminophenylthiocarbamide" read "aminophenylcarbamide."
687	4	„ "1899" read "1889."

* From bottom.

bromine is eliminated when bromodinitrobenzene is reduced to *m*-phenylenediamine by tin and hydrochloric acid (C. L. Jackson, *Amer. Chem. J.*, 1896, **18**, 466; Blanksma, *Rec. trav. chim.*, 1905, **24**, 320). Both these authors rightly supposed that bromine is only eliminated from the diamine. In support of this view, Jackson showed that bromophenylenediamine loses a bromine atom on treatment with tin and hydrochloric acid, but it might equally be removed from the dinitro-compound or from the nitroaniline. To show that such is not the case, the following experiments were carried out, which prove that if complete reduction by tin and acid in aqueous solution is replaced by partial reduction by stannous chloride and acid in alcohol, no bromine is eliminated.

(1) If bromine were removed from the bromodinitrobenzene or from the bromonitroaniline, the latter would contain nitroaniline. Accordingly, the amino-group was eliminated, whereby minute quantities of a nitroaniline may be detected by the odour of nitrobenzene and by the hypochlorite reaction of aniline after reduction (as was specially ascertained by a corresponding test with *m*-nitroaniline). No trace of nitroaniline was present. (2) If bromine had been removed, the neutralised stannic acid mixture would contain sodium bromide. Accordingly, after careful removal of the sodium salt of aminophenol by means of acetone, the inorganic mixture was tested for bromine, which was shown to be completely absent.

It was further ascertained that very little diamine is formed during these partial reductions of bromodinitrobenzene, the amount being, in expt. 40, less than 0.05 gram.

Finally, the action of alcoholic sodium acetate on bromodinitrobenzene was examined. On boiling for forty minutes, no reduction took place, but some bromine was displaced by hydroxyl, 0.03 gram of silver bromide being obtained, whilst the yellow solution contained some dinitrophenol in the form of its sodium derivative.

The dibromodinitroazoxybenzene obtained from expt. 48 was sparingly soluble in acetic acid, and crystallised from it in dark yellow crusts melting and decomposing at 160–180°.

Dichlorobromonitrobenzene.—In the preparation of this compound (compare Flürschheim, *loc. cit.*), the proportions were somewhat altered. Twenty-two grams of 2:6-dichloro-1-nitroaniline were dissolved in 450 c.c. of glacial acetic acid, and 88 c.c. of concentrated hydrobromic acid and 33 grams of sodium nitrite were added to the hot solution. When the evolution of nitrogen had ceased, the whole was cooled and poured into a little more than the same volume of water. The crude product weighed 28 grams, that is, almost the theoretical yield, and, after a single crystallisation from alcohol, showed the correct melting-point, 88°. On reducing the amount of acetic acid by one-third and

the hydrobromic acid by one-fourth, an equal yield of an almost equally pure product was obtained.

p-Nitrobenzaldehyde.—The following compounds were obtained in varying amounts:

(1) Unchanged nitrobenzaldehyde; (2) azoxybenzaldehyde; (3) polymeric aminobenzaldehyde hydrochloride; (4) anhydro-bases, formed by the condensation of aminobenzaldehyde with nitrobenzaldehyde and azoxybenzaldehyde.

Where the amine was not determined, the azoxyaldehyde was obtained by oxidising the total organic matter with permanganate and separating the azoxybenzoic acid from the nitrobenzoic acid by methyl alcohol. To ascertain that no azoxybenzoic acid was formed by the action of permanganate on aminobenzaldehyde, just as alkaline permanganate oxidises aniline to azoxybenzene, the oxidation was repeated in most cases with chromic acid in sulphuric acid, and practically identical results were obtained.

As concentrated solutions of chromic acid carry the oxidation too far, 1 part of chromic acid in 1.8 parts of sulphuric acid and 8 parts of water was used, which on boiling for a few minutes was found to convert *p*-nitrobenzaldehyde quantitatively into the acid. Accordingly, the mixture of aldehydes was dissolved in concentrated sulphuric acid, treated with finely-powdered sodium nitrite to prevent oxidation of the amino- to the azoxy-group, and then treated with chromic acid in the above proportions.

Further, it was ascertained that the alcohol used for precipitating the excess of permanganate does not transform nitrobenzoic acid into azoxybenzoic acid by alkaline reduction.

The estimation of the amine proved rather complicated. Reduction being at an end, the cooled solution was separated from the crystalline deposit (a mixture of nitro- and azoxy-benzaldehyde) and evaporated, then treated with sodium hydrogen carbonate, and extracted with ethyl acetate. The residue from the latter was treated with benzene, when a portion remained undissolved; it consisted mostly of polymeric aminobenzaldehyde, and in addition some anhydro-bases which yielded on oxidation an amount of nitro- and azoxy-benzoic acids corresponding with the nitro- and azoxy-aldehyde parts of the anhydro-base molecules. By deducting this portion from the total weight of the substance insoluble in benzene, the amine contained in the latter was obtained.

From the benzene solution, hydrogen chloride precipitated the hydrochlorides of anhydro-bases and polymerised aminobenzaldehyde, in which azoxy- and nitro-benzaldehydes were again determined by oxidation and deducted. The benzene filtrate then only retained azoxy- and nitro-benzaldehydes.

Polymeric aminobenzaldehyde and its red hydrochloride were identified by their characteristic behaviour, as was also the azoxybenzoic acid; the latter dissolved in sodium carbonate or pyridine with a marked yellow colour, and was precipitated by acids; it was practically insoluble in ordinary solvents, and did not melt.

Dinitrodiphenylamine.—In expt. 59, 1.05 grams of the dinitrodiphenylamine were recovered on evaporation of the filtrate from the precipitated amine. By fractional crystallisation and mixed melting-point tests, it was ascertained that no trace of an azoxy-compound was present. A similar result was obtained in expt. 60.

In conclusion, the authors wish to express their acknowledgment of the facilities placed at their disposal at the Davy-Faraday Research Laboratory of the Royal Institution, where the present work has been carried out.

CXLII.—*The Reduction of Refractory Oxides by Carbon.*

By HAROLD CECIL GREENWOOD, M.Sc.

THE chief object of this research was to determine the temperatures at which carbon begins to reduce some of the more difficultly reducible metallic oxides. Our knowledge of metallurgical reactions up to the temperatures attainable with ordinary fuel-heated furnaces is fairly complete. For instance, the temperatures of reduction of oxides such as those of copper, iron, and lead by carbon have been investigated by Wright and Luff (*Trans.*, 1878, 33, 1) on somewhat similar lines to the experiments here described, but only reductions occurring below 600° were studied. Again, the reduction of iron oxide by carbon under different pressures of carbon monoxide has been studied by Schenck, Semiller, and Falcke (*Ber.*, 1907, 40, 1704). Various other reduction temperatures have been investigated, but in nearly all cases the experiments have been confined to temperatures below 1000°.

On the other hand, thanks to the work of Moissan, we now have an extensive knowledge of the ultimate possibilities of effecting such reductions at extremely high temperatures varying up to that of the electric arc. Little, however, has been done to investigate the intermediate stages, or to control and adjust the electric heating in such a manner as to determine the lower limits of temperature at which such reactions commence. In quite early days, Sainte-Claire Deville greatly extended our knowledge of high temperature reactions by the use of

the oxy-hydrogen blowpipe, and now that such temperatures can be readily obtained in the laboratory, and accurately controlled so as to remain practically constant over long periods, there appears to be a wide field open for further investigation.

To take the case of the oxides of chromium and manganese, their reduction by carbon was accomplished by Deville (*Ann. Chim. Phys.*, 1856, [iii], 46, 182) in the oxy-hydrogen furnace, and consequently it is generally stated in text-books that a temperature approaching the melting point of platinum is essential.

The following experiments indicate, however, that the reduction commences far below this (chromium sesquioxide, 1105° ; manganous oxide, 1105°), and although it is possible that in practice a somewhat higher temperature would be necessary to effect complete reduction, considering the difficulties of ensuring uniform and intimate mixture, and the inverse reaction of the carbon monoxide, which would be well marked at atmospheric pressure, the difference is very great, and serves to emphasise the importance of the accurate investigation of this subject.

EXPERIMENTAL.

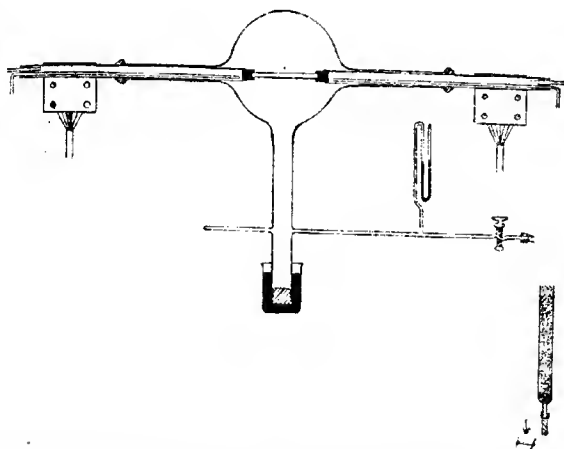
Apparatus.—The mixture of the oxide with carbon (except where otherwise stated, made as intimate as possible by rubbing together in an agate mortar) was filled into a small Acheson graphite tube generally about 10 cm. in length, and of 8 mm. external and 5 mm. internal diameter. In the first experiments a boat was made by grooving a rod of agglomerated gas carbon (compare Slade, *Trans.*, 1908, 93, 327), but it was found difficult to get a sufficient quantity of material in the groove, and, moreover, the temperature of the boat when heated was often much higher than that of its contents. The graphite tube which had a few perforations along the upper side to allow of the escape of gases was held in graphite plugs, the latter being soldered into water-cooled brass tubes after electro-coppering the ends. The brass tubes were fitted into the side arms of a glass globe of about $1\frac{1}{2}$ litres capacity as shown in Fig. 1, and a perfectly tight joint was made between the glass and the brass by means of a special wax. The heating of the carbon tube was effected by the passage of direct current (up to 300 amperes), which was led on to the water-cooled tubes.* An accurate control of the current was obtained by manipulation of a rheostat with fine adjustment in the exciting circuit of the dynamo used. The neck of the globe was closed by a rubber stopper with a mercury seal, and connexion was made through a tap and calcium chloride tube to a Fleuss pump, by means of which

* This type of apparatus was first described by J. N. Pring and R. S. Hutton (*Trans.*, 1906, 89, 1591).

the pressure could be quickly reduced to half a millimetre. Evacuation by a Töpler mercury pump was found to be much too slow, especially when carbon monoxide began to be produced. Before each experiment the apparatus was exhausted for several hours, a little phosphoric oxide being placed inside the apparatus to absorb water vapour. In many cases the carbon tube was heated to about 600° for a short time to assist the drying. The air was then re-admitted through the drying tube, the phosphoric oxide quickly removed, a little glass wool placed above the stopper in the neck to shield it from heat radiation, and the globe re-exhausted.

In the actual experiment the temperature of the graphite tube was

FIG. 1.



The graphite tube containing the mixture of the oxide and carbon is mounted inside an evacuated glass globe in graphite plugs soldered into water-cooled brass tubes. The latter serve as leads for the heating current and are luted into the side arms of the vessel.

raised fairly rapidly to a dull red heat, and then raised by small steps, careful measurements of the temperature being taken at each, until any desired value was attained.

Temperature Measurement.—Temperature measurements were made by means of the Wanner optical pyrometer, which was used with an ammeter and rheostat in circuit, and was frequently standardised. Apart from the question of deviation from black-body radiation it was thought possible that the temperature inside the carbon tube might be higher than that of the outer surface. To test this particular point, an experiment was carried out with a thermo-junction placed

inside the graphite tube. The couple wires were threaded through thin bent porcelain tubes passing through holes near the ends of the graphite tube (Fig. 2), and were brought down and cemented through two tubes passing through the stopper in the neck of the flask. (Before heating the carbon tube the apparatus was exhausted as in the reduction experiments.) Any leak of the heating current on to the thermo-couple wires would of course have been fatal to temperature measurements. Its absence was demonstrated by the fact that on suddenly applying the current when the tube was cold, or suddenly breaking the current when the tube was heated, no appreciable movement was noticed on the thermo-couple galvanometer.

As an additional safeguard, after taking a set of readings for different temperatures, the readings were repeated with the direction of the current reversed. No sensible difference, however, was observed between the two series of readings, so that the porcelain tubes seem to retain their insulating properties quite well up to 1300° . Between 900° and 1250° , the temperatures observed on the thermo-element inside the tube agreed reasonably well with those given by the optical

FIG. 2.



pyrometer sighted on the outside. The readings of the former were lower than those of the latter by slightly varying amounts, the maximum being 15° . It is, then, probable that the temperatures indicated by the optical pyrometer are rather higher (although by not more than about 10°) than the actual temperature inside the carbon tube; at any rate up to 1250° .

In the results which are to be found in the following pages, this correction has not been applied, as the experimental error is probably of about this order.

Method of Determining the Reduction Point.—The temperature at which reduction commenced was gauged by the commencement of the evolution of carbon monoxide from the mixture of oxide and carbon.

Interference of Gas Occluded by Carbon.—The most serious difficulty encountered was the fact that the carbon and the graphite tube contain occluded gas which is gradually given off as the temperature is raised. It was found, however, that if the temperature were raised in small steps and maintained constant for some time at each, the increment of pressure due to occluded gas in a given time was

practically constant for different temperatures. (In order to reduce the amount of occluded gas as far as possible, and to expel any moisture, the carbon and the graphite tube were generally given a short heating before use.) The method for estimating the rate of gas evolution finally adopted and followed in all the experiments consisted in maintaining the tube at a constant temperature for five minutes and observing the rise of pressure during the interval. At the end of each interval, the pressure was reduced by rapid evacuation during the next minute, and the temperature then raised to another value, at which it was maintained for five minutes, and so on. The rate at which gas is evolved from the carbon depends, first, on the difference in temperature between each step, and, secondly, on the length of time the carbon has been maintained at a constant temperature. Of course, the increase in pressure on raising the temperature is to some extent due to expansion as well as to the actual gas evolution. This effect, however, is approximately constant for each temperature step, and is only small, as the average temperature of the gas probably does not exceed 200° when the carbon tube is heated to 1500° .

To find the magnitude of the increment of pressure caused by occluded gas, a blank experiment was first carried out with a graphite tube filled with retort-carbon (a form of carbon used in most of the reduction experiments). For steps of about 80° over a temperature range of 900° to 2000° , the rise in pressure during five minutes varied from 2 to 4 mm. In the actual reduction experiments, as the mixture only contained a fairly small proportion of carbon and the temperature on nearing the reduction point was only raised in steps of 20° to 30° , the rise in pressure during five minutes seldom exceeded 2 mm.

Firing of Reduction Point.—When the reduction temperature of the oxide is attained, the gas evolution shows a marked increase. This is perhaps best shown by giving the experimental data for a typical experiment (with retort-carbon and chromium sesquioxide).

No. of successive 5 min. intervals.	Amperes.	Volts.	Temp.	Pressure risen in mm.		Rise of pressure.
				From	To	
1	110	3.5	930	3	4	.1
2	120	3.9	1014	2	4	2
3	130	4.2	1107	3	5	2
4	135	4.35	1134	3	5	2
5	140	4.50	1163	3	5	2
Reduction point.						
6	145	4.75	1195	4	14	10
7	150	4.85	1230	5	29	24
8	150	4.85	1230	6	24	18
9	150	4.85	1230	5	16	11
10	150	4.85	1230	5	12	7
11	150	4.85	1230	5	10	5

When the temperature is maintained constant a little above the reduction point, the gas evolution gradually dies away on account of the decrease of contact surface as reduction proceeds. As regards the fixing of the temperature at which reduction commences, the following convention was used: if there be a sharp jump from a pressure rise of, say, 2 mm. in five minutes to one of 10 or 20 (as in the above example), the reduction temperature is taken as the mean of the two temperatures, but if at three successive temperature steps the rises in pressure are such as 2, 5, 15, then the middle temperature is taken as that of initial action. With temperature steps of 20–30°, this method gives quite concordant results. On account of the reversible nature of the reaction between carbon and metallic oxides, the pressure of carbon monoxide present should have some influence on the reduction temperature. However, in these experiments the pressure of carbon monoxide when reduction commenced was practically constant, being in no case above 5 mm., so that any variation from this cause would be within the errors of temperature measurement.

Owing to the high thermal conductivity of graphite, the temperature of the tube was not uniform, but fell off towards the ends, the temperature being, however, quite sensibly uniform for 2–3 cm. in the centre. Consequently, when the temperature of the centre was only taken just above the reduction point, the reduction was confined to 2 or 3 cm. in the middle. This portion was extracted by breaking the tube, and its appearance under the microscope and its behaviour with various reagents investigated.

Reduction of Chromium Sesquioxide.

Details of Experiments.—To proceed to an account of the actual results, the oxide most carefully studied was chromium sesquioxide. Some preliminary experiments showed that reduction commenced at about 1200°. The material used was Merck's "extra pure" chromium sesquioxide, which was intimately mixed with a good quality retort carbon (the same sample being used throughout all the series of experiments) in approximately the theoretical proportions. The reduction temperatures estimated from three careful experiments with these materials were 1186°, 1185°, and 1195° respectively.

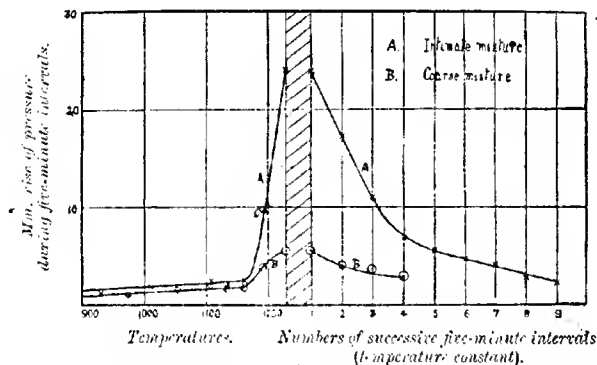
The product contained small globules of metallic appearance fairly uniformly distributed through the cross-section of the central portion. Quantitative reduction was never obtained on account of the limit to the intimacy of admixture attainable with retort carbon (the temperature not being taken much above the reduction point). The product effervesced vigorously with cold dilute hydrochloric acid, and the hydrogen evolved had an odour of hydrocarbons, so that probably the metal was somewhat carburised.

The manner in which the gas evolution falls off when the temperature is maintained constant a little above the reduction point was deemed worthy of further investigation.

Experiments on the Mechanism of the Reduction.—With an intimate mixture of chromium sesquioxide and retort-carbon the temperature was gradually raised to a value slightly above the reduction point (to 1230°) and maintained constant there, the increments of pressure during successive five-minute intervals being noted. The way in which the rise of pressure increases and then falls off is shown in Fig. 3 (Curve A).

Another experiment was next carried out under exactly similar conditions with a mixture of chromium sesquioxide and coarse retort-carbon in the same proportions as before. (The retort-carbon was a portion of the sample used in the other experiments, but with the

FIG. 3.



granules of such a size that they passed through a muslin sieve with 23 meshes to the inch, but not through one with 52.) In this case the pressure began to rise at about the same temperature, but the extent of the reaction was much more limited. Even on afterwards raising the temperature to 1300° the gas evolution was small. The great influence of this intimacy of mixture is shown in Fig. 3, and would seem to point to several important conclusions.

1. The temperature at which the gas begins to be evolved is that at which reduction by carbon takes place, and is not a mere precess of dissociation.*

* The dissociation of the oxides of vanadium, niobium, and tantalum in a vacuum was studied by W. von Bolton (*J. Soc. Chem. Ind.*, 1906, 25, 957), and that of the oxides of lead, bismuth, antimony, and cadmium by Pannu and Kraft (*Ber.*, 1907, 40, 4775).

2. The falling off of the gas evolution and the incompleteness of the reduction is due to the decrease of contact surface between oxide and carbon. In the experiment with the coarse carbon the reduction could be very plainly seen to be limited to the actual surface of the carbon granules, which were coated with a metallic mirror. This last fact also indicates that the reduction is really effected by carbon and not by any hydrogen or carbon monoxide present.

Effect of Different Varieties of Carbon.

It was also thought desirable to investigate the effect of different varieties of carbon, chromium sesquioxide again being a convenient oxide to use for the comparison. The carbon next tried was that obtained by the explosion of acetylene. This is a very pure carbon and at the same time is in an extremely fine state of division.

A. Acetylene Black.—A mixture was made in the theoretical proportions, the acetylene black being first made more compact by compressing into a glass tube. Here the temperature of reduction found was lower than that for retort-carbon and was specially well marked. For instance, in one experiment the increments of pressure in five minutes at 1100° and 1120° were 1 mm. and 57 mm. respectively. Three experiments done under similar conditions gave as reduction temperatures 1110° , 1105° , and 1100° . The gas evolution fell off rather quickly, and the cross-section of the product in the centre appeared to be quite homogeneous and metallic. No green chromium sesquioxide could be seen, and practically all the product dissolved in hydrochloric acid (chromium sesquioxide after ignition is almost unacted on by acids), so that the reduction appeared to have been practically complete, the maximum temperature having been 1120° . The completeness of the reaction, and perhaps to some extent the fact that the reduction temperature obtained is lower than that for retort-carbon, is due to the very perfect contact of carbon and oxide.

B. Purified Sugar Charcoal.—To determine whether the small amounts of ash or hydrogen in the form of carbon previously employed interfered with the reaction, an experiment was performed with purified sugar charcoal. This was finely pulverised and heated for about fifty hours in a current of chlorine at a temperature of over 1000° in a porcelain boat placed in a fused silica tube. It was subsequently heated for a short time in nitrogen, and finally in hydrogen. A portion gave an ash content of 0.04 per cent. This carbon was ground up with chromium sesquioxide in the usual proportion. With the object of expelling the occluded gas from the graphite tube, this was heated to 2000° for some time in a vacuum (in the reduction

apparatus) before filling with the mixture of oxide and carbon. The temperature of initial action in this case proved to be rather higher than that for retort-carbon, namely, 1240° . This may be to some extent due to the hardening of the carbon by the prolonged heating to which it was subjected before use.

Reduction Temperature of Manganous Oxide.

Manganous oxide was prepared by reduction of the higher oxides by hydrogen. For the first experiments the oxide was obtained in a more or less crystalline state by introducing a trace of hydrogen chloride into the hydrogen used for the reduction (Deville, *Compt. rend.*, 1861, 53, 199), the object being to render the product more stable in air. The manganous oxide was intimately mixed with retort-carbon in the theoretical proportions. The point at which carbon monoxide began to be evolved was very sharply defined—rather more so than with chromium sesquioxide. It was soon evident that samples of manganous oxide prepared in this way at different times did not give concordant reduction temperatures. For example, three different batches gave reduction points of 1200° , 1100° , and 1125° respectively. This discrepancy was not due to any experimental error, as different experiments with portions of the same batch gave results agreeing among themselves.

The conclusion arrived at was that the variation was due to differences in the physical state of the manganous oxide. Probably the exact state of the crystalline oxide varied with the temperature and other conditions of its preparation. It was afterwards found that the oxide could be obtained in a form quite stable in air without the use of hydrogen chloride by heating to a fairly high temperature in hydrogen. Another advantage of this simpler method of preparation is that the risk of contamination by chloride is avoided. Manganous oxide so prepared gave a reduction temperature of 1105° . This temperature would then seem to be the true reduction point for amorphous manganous oxide by retort-carbon. When reduction commences, a small mirror-like sublimate probably consisting of metallic manganese, which is a relatively volatile metal, always formed slowly on the globe. The residue on the central part of the graphite tube appeared to contain a good deal of metal. It effervesced vigorously with cold dilute hydrochloric acid and with boiling water. On treating with copper sulphate solution and examination under the microscope, the metallic globules originally white were seen to have become unmistakably copper-plated. A sample of the gas produced on solution of the residue in acid was analysed, and proved to contain 57 per cent. of hydrogen and 39 per cent. of methane. Considering this in conjunction with the known

action of acid on manganese and manganese carbide (Mn_3C), the calculated percentage of carbon in the metal is 6.

Reduction of Uranium Dioxide.

Black uranium oxide was reduced to the dull copper-coloured dioxide (UO_2) by strongly heating in hydrogen. Two experiments with a mixture of this oxide and retort-carbon indicated reduction temperatures of about 1480° and 1500° respectively. The central reduced portion of the residue was found to have become of much darker colour, and was caked hard together. The unchanged mixture from the ends of the graphito tube was unaffected by hydrochloric acid, but the central portion effervesced briskly on warming (giving an odour of hydrocarbons) and slowly decomposed boiling water. The presence of metal was not easily recognised by microscopic examination, probably because of the high melting point of uranium. One experiment carried out incidentally with uranium dioxide dealt with the effect of a large excess of carbon. A mixture of the oxide with carbon was made in the proportions 2 to 1, the proportion (theoretical) used in the other experiments being 11 to 1. However, the excess of carbon seems to make little difference to the temperature at which reduction commences (about 1490°), although of course it decreases the amount of gas evolution by diminishing the quantity of oxide present.

Reduction of Silica.

The action of carbon on silica was next studied. Pure precipitated silica was first used and mixed intimately with retort-carbon in the proportion $\text{SiO}_2 : 2\text{C}$. A sudden rise of pressure occurred at about 1480° , when a slight sublimate formed. As the silica used was very light and voluminous not much residue was left, so the experiment was repeated, using white sand which was purified by finely pulverising and boiling with concentrated hydrochloric acid. Reduction commenced at about 1460° and a slight sublimate appeared as soon as the reduction had become marked. The residue, which under the microscope appeared to consist of yellowish crystals, was unaffected by sodium hydroxide solution except a portion from the extreme cold ends of the tubes which effervesced vigorously for a short time, denoting the presence of a little silicon or silicon monoxide (Potter, *Trans. Amer. Electro. Chem. Soc.*, 1907, 12, 191), which had volatilised and escaped carburisation. The central portion, after igniting in air, to burn off the carbon, and then extracting several hours with hot hydrofluoric acid, left a large greenish-grey residue. This on heating to dull redness in chlorine glowed and left a black residue of carbon. On strongly heating a small quantity in chlorine for a considerable

time, no precautions being taken to exclude all oxygen, the substance entirely disappeared, being evidently silicon carbide or oxycarbide (siloxidon).

Tucker (*J. Amer. Chem. Soc.*, 1906, 28, 853), by determining the temperatures of different layers in a carborundum furnace, estimated the temperature of formation of the oxycarbide to be somewhere in the neighbourhood of 1600°. As the operation was carried out under atmospheric pressure, the inverse reaction of the carbon monoxide probably exerts a considerable effect on the temperature of reaction.

The reduction temperatures of a few other oxides were also studied, retort-carbon and the finely powdered oxide being used.

Zirconia.—With this oxide reduction commenced fairly sharply about 1400°. The amorphous black product seemed to be carbide: it glowed on heating gently in chlorine.

Thoria.—This oxide gave the highest reduction temperature studied in these experiments, namely, about 1600°. The yellowish-grey product was carbide, giving a brisk effervescence with cold water. (The presence of metallic iron was found to have no appreciable lowering effect on this reduction.)

Tungsten Oxide.—Brown tungsten dioxide was prepared by heating the trioxide to dull redness in hydrogen, and mixed in the theoretical proportions with retort-carbon. Two experiments both gave sharp reduction points at about 1020°. In one experiment the temperature was only raised to 1115°, and the resulting product seemed quite metallic.*

Experiments on the Dissociation of Oxides in a Vacuum.

The experiments described on page 1489 dealing with the effect of using a coarse carbon for the reduction made it appear very improbable that the observed temperature of reduction was merely a dissociation in vacuum. In order to leave no doubt on this question the following experiments were carried out.

A trace of the oxide to be studied was placed on a platinum ribbon† 5 mm. wide, soldered to water-cooled leads, and fitted inside an apparatus similar to but smaller than that used for the reduction experiments. A high vacuum was obtained by the use of a charcoal tube cooled in liquid air. The strip was heated by gradually increasing currents, the current being maintained constant at each

* According to Dammer the reduction temperature of tungsten trioxide by carbon to metal (at atmospheric pressure) is above the melting point of nickel (1427°).

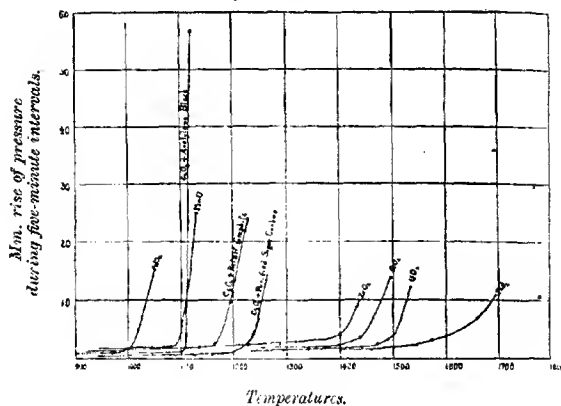
† The melting points of the elements of the iron group were determined in a similar manner by G. K. Burgess (*Bull. Bureau of Standards*, Reprint No. 32).

step for about ten minutes, cooled down in the interval, and the residue examined by a microscope. The "black-body" temperature was determined by the Wanner pyrometer, and the necessary correction for the departure from perfect "blackness" applied.

Experiments with Manganous Oxide.—After heating to a temperature of 1400° , the oxide was certainly unaffected except that the green colour was perhaps a little more intense. Just about 1460° , however, the traces of green oxide were (after cooling) seen to have collapsed, leaving metallic-looking spots. This change takes place quite definitely and sharply if a very minute quantity of the oxide is used. No definite indication of any melting of the oxide before reduction was observed.

Manganous oxide was found to be oxidised by heating under a

FIG. 4.



pressure of 1 mm. of air, the green colour being, however, restored on heating in the high vacuum.

These experiments show quite conclusively that manganous oxide undergoes no dissociation at its temperature of reduction by carbon, namely, 1100° .

Uranium Oxide.—With this oxide the indications were much less definite, but a similar kind of dissociation would appear to take place in the neighbourhood of 1600° .

Chromium Sesquioxide.—In this case practically no effect seemed to be produced by heating in a high vacuum to near the melting point of the platinum strip. The oxide on cooling had become slightly darker in appearance, but seemed to be otherwise unaffected. It is, however,

quite certain that chromium sesquioxide does not undergo the slightest dissociation at its reduction temperature by carbon.

Tungsten Dioxide.—Tungsten trioxide on heating, to successively higher temperatures becomes first dark blue (W_2O_5) at about 1250° , and then brown (WO_2) at about 1350° . At a temperature of about 1450° a fairly sharp change takes place, the brown oxide almost disappearing. One may conclude, therefore, that tungsten dioxide does not exhibit the slightest tendency to dissociation at its reduction point (1010°).

Experiments on the Dissociation of Oxides in Air at very High Temperatures.

A series of experiments was now carried out in the open air, using an iridium strip soldered on to water-cooled tubes. The radiation correction for the temperature readings was assumed to be the same as that for platinum and palladium.

Chromium Sesquioxide.—This was quite unaffected after heating to 1640° . About 1700° the trace of oxide after cooling began to have in some places a darker colour and a more or less crystalline appearance. This change gradually progressed as the temperature was raised, some shrinking taking place. When the temperature had been raised to about 2000° , the residue on cooling appeared quite metallic, and a distinct effervescence took place on moistening with a drop of hydrochloric acid under the microscope.

An experiment with purified sand showed that at about 1750° the crystalline particles lost their shape (fairly sharply) and became semi-fused.

In the case of the oxides of manganese, chromium, tungsten, and silicon studied, there is thus no doubt that at their reduction temperatures, the phenomenon of dissociation plays no part. This appears to be also true for uranium, although the evidence in this case is not quite so clear.

Summary.

(1) A method has been worked out for measuring with accuracy the temperatures of reduction of refractory metallic oxides by carbon, the apparatus devised being suitable for use up to at least 2000° , and being capable of maintaining the temperature constant to within about 10° .

(2) It is shown that the oxides of chromium (1185°), manganese (1103°), uranium (1490°), silicon (1469°), zirconium (1400°), and thorium (1600°) are reducible by carbon at temperatures far below those which are generally supposed to be necessary for the production of these metals from the oxides.

(3) These reductions commence very sharply at a given temperature, but the progress of the reduction depends greatly on the intimacy of contact and thus on the degree of subdivision of the oxide and carbon.

(4) The reduction temperature is found to alter on using different varieties of carbon. In some cases differences are also indicated between samples of the oxide prepared under varying conditions, but the effect can be shown to be due to the physical state of the oxide.

(5) In all the cases studied the reaction takes place long before the melting point of the oxide is reached, and the product of reduction is also in the infused state.

(6) Experiments to measure the temperature of dissociation of these oxides indicate that they are extremely stable (even in a high vacuum) up to temperatures far exceeding the reduction point by carbon.

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CXLIII.—*The Production of Ferro-alloys.*

By HAROLD CECIL GREENWOOD, M.Sc.

It is a well-known fact that whilst it is very difficult to produce elements such as chromium and silicon by direct smelting of the oxides, the production of ferro-alloys from a mixture of the oxides with ferric oxide is a comparatively simple matter. To account for this behaviour several causes can be suggested.

(1) Greater fusibility of the alloy and consequent agglomeration of the reduction product into a mass escaping re-oxidation or back reaction.

(2) That the local increment of temperature due to the oxidation of carbon by the ferric oxide might raise the temperature of the neighbouring particles of the more refractory oxide to that required for reduction.

(3) Some definite chemical affinity between the two metals. Some experiments conducted with silica led to a somewhat lengthy investigation of the problem. The temperatures of reduction of certain oxides by carbon in the presence of metallic iron and other substances were studied, the apparatus used being that described in the preceding paper.

Influence of Iron on the Reduction of Silica.—A preliminary experiment using a mixture of purified sand, retort-carbon, and electrolytic iron powder in the proportion 20:8:30, respectively, indicated that

reduction commenced at a much lower temperature (about 1200°) than with silica and carbon alone (1460°). This fact seemed so striking that the matter was closely investigated.

The product of the experiment, in which the temperature was raised to 1300° , was found to be only slowly attacked by boiling concentrated hydrochloric acid (unlike pure metallic iron). No appreciable magnetic separation could be effected. After a short ignition in air to remove carbon, the central portion was practically completely soluble in warm hydrofluoric acid, consequently it did not contain silicon carbide. On account of the great inertness of iron silicide it was found very difficult to establish the presence of silicon in this form. The only method at all satisfactory was to heat a small quantity to dull redness in chlorine, and test if silicon chloride was produced. The exit gases were passed through sodium hydroxide solution, which was filtered from any ferric hydroxide produced by ferric chloride volatilising over, acidified, and ammonium hydroxide added. With the above residue a very distinct gelatinous precipitate was produced. The objection to this method is that a mixture of silica and carbon is known to give silicon chloride on heating to a rather high temperature in chlorine. However, a blank experiment with a mixture of iron, silica, and carbon (the iron being added so that the effect of the rise of temperature due to the combustion of the metal might be the same in both cases) treated in a similar manner gave no precipitate of silica, so that it may be concluded that iron silicide was present in the former mixture.

On repeating the reduction experiment more carefully, the gas evolution seemed to commence at a rather lower temperature, namely, about 1100° . In another experiment, using the finely-divided iron obtained by reducing ferric oxide in hydrogen at a dull red heat, reduction commenced about 1050° . The temperature was maintained at 1140° for some time, and the resulting product warmed in chlorine, when silicon chloride was obtained, showing the presence of iron silicide as in the first experiment. (To ascertain if the iron used contained any oxide, an experiment was carried out with this metallic iron mixed with carbon, but no evolution of gas in quantities sufficient to interfere with the above experiment was noticed.)

These experiments leave no doubt that the presence of metallic iron exercises a remarkable influence on the reaction between silica and carbon. The exact temperature at which action commences is, as might be expected, not so sharply defined as in the simple reduction of an oxide. The experiments would also point to the conclusion that in the reduction of a mixture of the oxides of iron and silicon the influence of the iron is exerted after reduction (which takes place at a comparatively low temperature) and not through the heat developed in the process.

Influence of Ferric Oxide on the Reduction of Silica.—With the idea of gaining more light on this point, an experiment was carried out with a mixture of silica, retort-carbon, and ferric oxide.

In this case, it is, of course, impossible to ascertain anything about the reduction of silica from the gas evolution. The temperature having been raised to 1130° , the product was heated in chlorine as before when only a slight turbidity due to silica was obtained. This would indicate that ferric oxide does not exert any appreciable influence on the reduction of silica before itself undergoing reduction. The fact that the reduced iron had produced so little reduction was probably due to its poor contact with silica.

Effect of Metallic Manganese on the Reduction of Silica.—The effect of metallic manganese was also investigated. With an intimate mixture of purified sand, retort-carbon and metallic manganese (free from aluminium and sodium), reduction commenced pretty sharply about 1100° ,* the temperature being raised to 1200° . After heating the product (which was hard and crystalline) in chlorine, and testing for silicon chloride as with iron, a marked precipitate of silica was obtained. (A blank experiment with a mixture of silica, carbon and manganese gave no such indication.)

Effect of Copper on the Reduction of Silica.—It was hoped that by using a mixture of purified sand, retort graphite and copper powder, it might be possible to collect any silicon formed by its solution in the molten copper. Reduction commenced at about 1250° , and the temperature was raised as far as 1340° . The result, however, was disappointing, as the copper had not fused together, but a grey residue was left which was only attacked with difficulty by nitric acid—the copper having probably formed silicide.

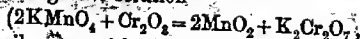
Referring to the three suggested causes for the influence of the presence of ferric oxide on the reduction of oxides by carbon, these experiments seem to show that local raising of temperature by reduction of ferric oxide does not play an important part. Probably direct affinity between silicon and the metal accounts for a good deal of the action, especially as the products (with iron, copper and manganese) were only difficultly fusible.

Influence of Iron on the Reduction of Chromium Sesquioxide.—The above experiments with silica led to an investigation in a similar way of some other oxides from which ferro-alloys are produced technically.

Starting with chromium sesquioxide, a mixture with retort-carbon and metallic iron (electrolytic powder) was taken. Contrary to the experience with silica, the mixture behaved just as if iron were absent, giving a sharp reduction point of 1190° . It was found possible to

* Reduction temperature in absence of manganese is 1460° .

separate the metallic portion of the residue from unchanged oxide by boiling with permanganate solution



this proceeds easily even with chromium sesquioxide which has been strongly heated), filtering, washing the residue with an alkaline solution of hydroxylamine hydrochloride to reduce the manganese dioxide, and then quickly washing with very dilute sulphuric acid and water. The acid easily dissolves the manganous oxide without much action on the metallic portion, which on drying seems quite free from chromium sesquioxide or any other oxides.

Effect of Ferric Oxide on the Reduction of Chromium Sesquioxide.—On the supposition that ferric oxide might have some specific action, an experiment was performed using a mixture of retort-carbon with ferric oxide and chromium sesquioxide, the temperature being raised to 1130°. Curiously enough, the residue was yellowish-brown and was unaffected by acid (except for the metallic iron present) and by boiling with permanganate. Thus it was not found possible to isolate the metallic portion (which, moreover, seemed to be present only in small quantity). Probably what had happened was that ferric oxide was first reduced to ferrous oxide, which combined with chromium sesquioxide to form the brown spinel ($\text{FeO}, \text{Cr}_2\text{O}_3$), only the excess of ferrous oxide being further reduced to metal.

Judging from these experiments, neither iron nor its oxides facilitate the reduction of chromium sesquioxide below its ordinary reduction temperature. At higher temperatures, the solvent action of the iron may have some effect in preventing re-oxidation.

Effect of Metallic Manganese on the Reduction of Chromium Sesquioxide.—Using instead of iron a mixture of metallic manganese with chromium sesquioxide and retort-carbon, reduction seemed to commence about 1120°.* The temperature was only raised to 1150°, but the residue on examination appeared to contain very little unreduced chromium sesquioxide. Another experiment in which the temperature was only raised to 1140° gave a similar result. On extracting the metallic portion by boiling with permanganate and treating as in the iron-chromium oxide experiments, the product appeared quite free from chromium sesquioxide under the microscope, and dissolved in hydrochloric acid to a bright green solution evidently containing a high percentage of chromium.

There is then little doubt that the presence of metallic manganese to some extent facilitates the reduction of chromium sesquioxide by carbon.

Effect of Iron on the Reduction of Manganous Oxide.—On heating

* Reduction temperature in absence of manganese = 1185°.

manganous oxide (the oxide reduced in pure hydrogen being used) with retort-carbon and electrolytic iron, the gas evolution became very marked at 1030° ; * the temperature was raised to 1055° . The metallic portion, which had slightly fused, was isolated by washing with dilute sulphuric acid, when manganous oxide is much more easily attacked than the metal. The residue under the microscope appeared quite free from any green oxide, and on testing gave the reactions of manganese. (A blank experiment with a mixture of manganous oxide and iron treated in the above way gave only an extremely faint coloration on boiling the solution of the metallic residue with lead peroxide and nitric acid.) In this case, then, iron appears to exert some influence on the reduction.

The alloys formed by chromium and manganese with iron are more fusible than the silicon alloys, so that the part played by the solvent action of the iron may be rather greater than with silica.

Finally, I wish to express my thanks to Dr. R. S. Hutton for suggesting the above investigation, and for much useful advice during its progress.

* Reduction temperature in absence of iron = 1105° .

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CXLIV.—*The Proteins of Egg-yolk.*

By R. H. ADERS PLIMMER, D.Sc.

IN 1900 T. B. Osborne and G. F. Camphell (*J. Amer. Chem. Soc.*, 1900, 22, 413) described an alternative method to the one usually employed for preparing vitellin from egg-yolk, which consisted in dissolving the yolk in 10 per cent. sodium chloride solution, extracting the lecithin and fat by shaking with ether, and then dialysing, or pouring the solution into a large volume of water, whereby the vitellin is precipitated. By re-solution in sodium chloride solution and reprecipitation by water, followed by extraction with alcohol and ether to remove lecithin, the vitellin was obtained in a state of comparative purity.

On repeating this process it was observed that, after complete precipitation of the vitellin by water, the aqueous solution gave a very marked biuret reaction, and that, on boiling and slightly acidifying

with acetic acid, a large precipitate of coagulated protein was formed. This was at first regarded as unprecipitated vitellin, but a phosphorus determination at once showed its non-identity with this protein, for it contained 0.1 per cent. of phosphorus compared with 1.0 per cent. in vitellin. It seemed scarcely possible that this coagulable protein was identical with ovalbumin present in the yolk, since ovalbumin is coagulated by ether, and since it contained less nitrogen than does ovalbumin; consequently it was necessary to regard it as a second and as yet undescribed protein in the yolk of eggs.

As it is impossible to decide upon the identity or non-identity of two proteins from the figures obtained by ultimate analysis, and as differentiation by hydrolysis into the constituent amino-acids requires a considerable amount of material, and, moreover, is as yet not sufficiently quantitative in its results to arrive at a decision, recourse was had to the determination of the various forms, in which the nitrogen is contained in the proteins. This method was first carried out by Hausmann, and has been used by several investigators, more especially by Osborne and Harris (*J. Amer. Chem. Soc.*, 1903, 25, 323) in their study of the vegetable proteins which showed distinct differences. Vitellin and this new protein showed a very close similarity to one another, but they differ considerably from ovalbumin, and it may be concluded that this protein is another constituent of egg-yolk. It is suggested that the protein may be vitellin without the phosphorus-containing portion and that it be provisionally named *livetin*.

The presence of another protein in egg-yolk is mentioned in Hammarsten's *Lehrbuch der physiologischen Chemie*, 6th edition. Gross,* by precipitation with ammonium sulphate, obtained a protein differing widely in composition from vitellin.

EXPERIMENTAL.

I. Twenty-five egg-yolks were mixed with about an equal volume of 10 per cent. sodium chloride solution, and extracted several times with ether until the ether separated without colour. The saline solution was then reddish in colour and almost transparent. It was poured into about twenty volumes of water, and after twenty-four hours the liquid was decanted from the precipitate of vitellin. For purification, this was redissolved in 10 per cent. sodium chloride solution, reprecipitated by water, and the process once more repeated. It was finally dissolved in very dilute sodium hydroxide, filtered and precipitated by acetic acid. After thoroughly washing with water, boiling with alcohol and ether to remove lecithin, and drying over sulphuric acid, the

* *Inaug. Diss.*, to which I have been unable to refer.

vitellin was obtained as an almost white powder; it weighed 31 grams. For analysis the substance was dried at 110° .

0.9242 gave 0.02802 P_2O_5 . * $P=1.1$.

0.2074 „ 0.03192 N_2 .† $N=15.39$.

0.2322 „ 0.03528 N_2 . $N=15.19$ per cent.

The aqueous solution from which this vitellin was precipitated gave a very marked biuret reaction, but no further precipitate on dilution; when heated to boiling in the presence of a small quantity of acetic acid, a coagulation occurred. The whole quantity was therefore filtered, and in several portions was heated to boiling, each portion being slightly acidified with acetic acid. The several portions of coagulated protein were collected together on a filter, thoroughly washed with water, boiled with alcohol and ether to remove lecithin, and dried over sulphuric acid, when 30 grams of an almost white powder were obtained. It gave the following results on analysis, for which a portion was dried at 110° .

0.5676 gave 0.001395 P_2O_5 . $P=0.11$.

0.2514 „ 0.03808 N_2 . $N=15.15$.

0.2876 „ 0.0434 N_2 . $N=15.09$ per cent.

This coagulated protein thus contains about the same amount of nitrogen as does vitellin, but the amount of phosphorus is very different. It must therefore be regarded as not identical with vitellin.

It has recently been found by Kaas (*Monats.*, 1906, 27, 403) and by Willcock and Hardy (*Abstr.*, 1907, i, 366) that ovalbumin contains 0.13 per cent. of phosphorus, and I have specially confirmed this with a specimen of crystallised ovalbumin prepared by Hopkins' method:

0.9356 gave 0.00228 P_2O_5 . $P=0.11$ per cent.

In spite of this similarity in the phosphorus content, it seemed scarcely possible that these two proteins could be identical, since ovalbumin is coagulated by ether, whereas livetin is not coagulated. The following experiment with carefully washed yolks was therefore undertaken to determine this, and in order to confirm the above result.

II. Thirty-two egg-yolks were singly thoroughly washed free from adherent egg-white by allowing a gentle stream of water to flow over them when held in the palm of the hand. They weighed 548 grams, and were mixed with an equal volume of 10 per cent. sodium chloride solution. As before, this saline solution was extracted with ether

* The estimations of phosphorus were all made by Neumann's method as modified by Plimmer and Bayliss (*J. Physiol.*, 1906, 33, 441).

† All the nitrogen estimations described in this paper were carried out by Kjeldahl's method.

until the ether was colourless, but instead of being poured into a large volume of water it was dialysed for twenty-four hours; at the end of this time a large precipitate of vitellin formed; this was separated from the aqueous solution which was again dialysed for twenty-four hours, whereby the last traces of vitellin were thrown down. The precipitate of vitellin was purified as in Experiment I, and 42 grams of lecithin-free material were obtained. The analysis was carried out with a portion dried at 110° :

0.4636 gave 0.01445 P_2O_5 . $P = 1.14$.
 0.2900 „ 0.04354 N_2 . $N = 15.01$.
 0.2070 „ 0.03094 N_2 . $N = 14.94$ per cent.

As before the aqueous solution was filtered and heated in several portions to 100° , when coagulated protein separated in the form of flakes, commencing at about 60° , and being complete at about 90° . The collected portions were washed, boiled with alcohol and ether, and dried over sulphuric acid; the yield of livetin in this case was 10 grams, and just as in the first experiment it contained 0.1 per cent. of phosphorus, as shown by the analysis:

0.8750 gave 0.00203 P_2O_5 . $P = 0.10$.
 0.3730 „ 0.05544 N_2 . $N = 14.86$.
 0.3050 „ 0.04592 N_2 . $N = 15.05$ per cent.

III. A third experiment was carried out exactly as described above with twenty egg-yolks; 16 grams of vitellin and 11 grams of livetin were obtained, which gave the following results on analysis:

Vitellin III.

0.5900 gave 0.0142 P_2O_5 . $P = 1.05$.
 0.2486 „ 0.03752 N_2 . $N = 15.09$.
 0.1972 „ 0.02926 N_2 . $N = 14.84$ per cent.

Livetin III.

0.8956 gave 0.00216 P_2O_5 . $P = 0.11$.
 0.3294 „ 0.04886 N_2 . $N = 14.83$.
 0.2116 „ 0.03136 N_2 . $N = 14.82$ per cent.

IV. It was now necessary to determine whether livetin existed in egg-yolks as such or whether it resulted by the action of sodium chloride on vitellin. Fourteen washed egg-yolks (= 254 grams) were therefore extracted with fresh quantities of ether until the ether separated almost without colour. The residue was then extracted three times with about 2 litres of water; the second extract only contained a small quantity of protein, whilst the third extract was free from protein. The first aqueous extract was filtered and heated to boiling in slightly acid solution, when a coagulum was formed. This was washed with water, boiled with alcohol and ether to remove lecithin,

and dried over sulphuric acid (yield = 6 grams). Analysis was carried out with material dried at 110° :

0.9376 gave 0.001395 P_2O_5 . $P = 0.65$.
 0.3354 „ 0.05026 N_2 . $N = 14.98$.
 0.3620 „ 0.05404 N_2 . $N = 14.93$ per cent.

The residue was dissolved in dilute sodium hydroxide, filtered, and precipitated by acetic acid. This process was repeated, and 12 grams of vitellin were obtained after boiling with alcohol and ether, and drying over sulphuric acid. For analysis, a portion was dried at 110° :

0.6470 gave 0.01268 P_2O_5 . $P = 0.85$.
 0.3028 „ 0.04648 N_2 . $N = 15.35$.
 0.3530 „ 0.05404 N_2 . $N = 15.31$ per cent.

V. Twenty-one washed egg-yolks (= 436 grams) were treated exactly as in experiment IV. Ten grams of vitellin and 7 grams of livetin were obtained of which the following are the analyses:

Vitellin V.

0.3664 gave 0.0085 P_2O_5 . $P = 0.99$.
 0.3284 „ 0.05068 N_2 . $N = 15.43$.
 0.2764 „ 0.04242 N_2 . $N = 15.35$ per cent.

Livetin V.

1.0316 gave 0.0014 P_2O_5 . $P = 0.59$.
 0.3338 „ 0.05082 N_2 . $N = 15.22$.
 0.3196 „ 0.04802 N_2 . $N = 15.02$ per cent.

The percentage of phosphorus in the preparations of livetin IV and V is considerably greater than in the preparations I, II, III. This may be due to a slight solubility of vitellin in water in the presence of livetin, which would consequently increase the amount of phosphorus in these preparations; it is scarcely possible that vitellin is separated into a phosphorus-containing portion and a phosphorus-free portion by the action of 10 per cent. sodium chloride solution as used in the first preparations, for under these conditions the amount of phosphorus in vitellin would be greater than 1 per cent., and, further, when the vitellin is purified by re-solution in sodium chloride solution and re-precipitated, no protein coagulable by heat is found in the water. The former method is therefore the better one for separating the two proteins.

The yields of vitellin and livetin obtained in the various preparations fluctuated considerably; in the first preparation, they were respectively 31 and 30 grams or almost equal amounts; in the other preparations, the yield of livetin was considerably less than that of vitellin. This difference suggests a close relationship between the two

proteins in the yolk of eggs, and it is emphasised by the preparations containing almost exactly the same amount of nitrogen, which is very different from that in ovalbumin, and also excludes the identity of livetin with ovalbumin. Ovalbumin, according to Osborne and Harris, contains 15.51 per cent. of nitrogen.

In order to determine the relationship of these two proteins in the yolk of egg more closely, the preparations were hydrolysed into their constituent amino-acids, and the various forms in which the nitrogen is contained—namely, amide-nitrogen, humin-nitrogen, diamino-nitrogen, monoamino-nitrogen—was estimated by Hausmann's method in the manner described by Osborne and Harris in their study of the vegetable proteins.

About one gram of each preparation was hydrolysed by boiling with 20 c.c. of concentrated hydrochloric acid for seven to ten hours. The solution was evaporated in a vacuum at 40° to remove free hydrochloric acid, the residue treated with about 300 c.c. of water, and a slight excess of magnesia, freed from ammonia by boiling, was added. This mixture was distilled in a vacuum at 40° and the ammonia (=amide-nitrogen) estimated. The solution was then filtered; the residue was thoroughly washed with water, and the nitrogen contained in it (humin-nitrogen) estimated by Kjeldahl's method. The filtered solutions and washings were concentrated on the water-bath to 100 c.c., allowed to cool, and precipitated with 30 c.c. of phosphotungstic acid solution (20 grams of phosphotungstic acid and 5 grams of sulphuric acid per 100 c.c. of water). The precipitate was filtered off after twenty-four hours and washed three times with a solution of phosphotungstic acid containing 2.5 grams of phosphotungstic acid and 5 grams of sulphuric acid in 100 c.c. of water, the washing being effected by rinsing the precipitate from the filter into a beaker and returning to the filter paper three times, each portion of the wash water being allowed to drain away completely before the next was added. The nitrogen was determined in the precipitate (=diamino-nitrogen) by Kjeldahl's method and the nitrogen in the filtrate (=monoamino-nitrogen) calculated by difference of these values from the total nitrogen of the preparations. Two experiments were carried out in each case, and for comparison two experiments were performed with caseinogen (Merck), the other well-defined phosphoprotein. The results are embodied in the following table, in which are also given the values obtained by Osborne and Harris for ovalbumin.

	Total nitrogen	Amide nitrogen	Histo- nitrogen	Essential nitrogen	Monoamino- nitrogen (by difference)
Livetin I...	15.15 15.39 } 15.12	0.78 0.71 } 0.75	0.37 0.26 } 0.32	3.28 3.32 } 3.29	10.73
Vitellin I...	15.39 15.19 } 15.29	0.86 0.81 } 0.84	0.23 0.28 } 0.25	3.85 3.84 } 3.84	10.26
Livetin II.	14.86 15.05 } 14.96	0.68 0.59 } 0.64	0.44 0.34 } 0.39	3.17 3.46 } 3.32	10.61
Vitellin II.	15.01 14.94 } 14.98	0.78 0.89 } 0.84	0.29 0.27 } 0.28	3.48 3.49 } 3.48	10.38
Livetin III	14.83 14.82 } 14.83	0.87 0.76 } 0.82	0.32 0.27 } 0.29	3.23 3.17 } 3.20	10.52
Vitellin III	15.09 14.84 } 14.97	0.89 0.93 } 0.91	0.26 0.26 } 0.26	3.35 3.34 } 3.34	10.43
Livetin IV.	14.38 14.93 } 14.96	0.66 0.69 } 0.68	0.28 0.25 } 0.26	3.09 3.15 } 3.12	10.99
Vitellin IV	15.35 15.31 } 15.33	0.69 0.80 } 0.75	0.26 0.25 } 0.25	3.78 3.76 } 3.77	10.56
Livetin V..	15.22 15.02 } 15.12	0.67 0.68 } 0.68	0.27 0.24 } 0.26	3.12 3.50 } 3.31	10.87
Vitellin V.	15.43 15.35 } 15.39	0.76 0.83 } 0.79	0.40 0.25 } 0.32	3.82 3.74 } 3.78	10.50
Caseinogen.	15.25 15.36 } 15.30	1.55 1.49 } 1.52	0.20 0.23 } 0.22	3.16 3.23 } 3.20	10.36
Ovalbumin (Osborne & Harris).	15.51	1.34	0.29	3.30	10.58

As can be seen from the table, distinct differences are noticeable between the values obtained for vitellin and livetin for the same preparation, although they are very close to one another. These differences are most marked in the monoamino-nitrogen figures, which are considerably higher for livetin than for vitellin. The opposite is the case for the amide-nitrogen and the diamino-nitrogen figures.

The several preparations of both vitellin and livetin do not give exactly the same figures; this is probably due to the impossibility of preparing a protein in a state of purity, in consequence of which some investigators, such as E. Fischer, consider a protein as made up of a mixture of complex substances which cannot be separated. If the complexity of a protein be considered, the same protein may not always be built up by the cells of amino-acids in exactly the same proportions. In the case of eggs, it must be remembered that greater or smaller changes in development occur before they are available for examination. This may also account for the different yields which were obtained, and it is possible that both vitellin and livetin represent stages in the change of a single original protein in the egg-yolk.

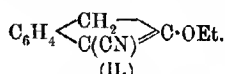
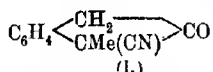
It may, however, be concluded that egg-yolk contains two proteins, which are fairly closely related to one another, the one, vitellin, containing 1 per cent. of phosphorus, and the other, livetin, containing 0.1 per cent. of phosphorus.

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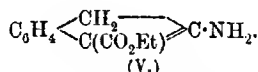
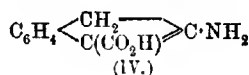
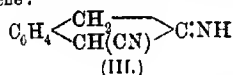
(XLV.—*The Action of Bromine on β -Hydrindone.*)

By NORMAN ALLEN CREETH and JOCELYN FIELD THORPE.

In a communication (Trans., 1908, 93, 165) dealing with the preparation and reactions of β -hydrindone, it was shown that the α -carbon atom of this substance cannot apparently carry a group of more than a certain molecular weight or volume, and that if a group greater than this is introduced the compound exists as a derivative of hydroxyindene. Thus, whereas α -cyano- α -methyl- β -hydrindone (I) exists as a true ketone, the corresponding ethyl derivative cannot be prepared in this form, but always occurs as 3-cyano-2-ethoxyindene (II):



Attention was also drawn to the same phenomenon in the case of β -iminohydrindene and its derivatives, for whereas β -imino- α -cyanohydrindene (III) is a true imino-compound, the corresponding carboxylic acid (IV) and its ethyl ester (V) are derivatives of 2-aminoindene:

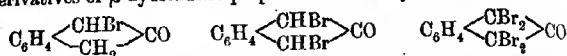


It was suggested at the time that these instances of "steric inhibition" in all probability depended on the molecular weights or a function of the molecular weights of the groups uniting with the α -carbon atom, and in order to ascertain whether the actual weights of the groups as distinct from their volumes were the determining cause of the inhibition, experiments were tried in which the effect of the introduction of a heavy atom such as bromine on the molecule of β -hydrindone was closely studied.

It was found that β -hydrindone is brominated very readily in chloroform solution, and that the bromination proceeds quite normally, yielding ultimately $\alpha\alpha\gamma\gamma$ -tetrabromo- β -hydrindone. The monobromo- and *sym.*-dibromo-derivatives are also easily prepared when the correct quantity of the chloroform solution of bromine is used. It was found, however, that instead of the tribromo-derivative being formed when the calculated quantity of bromine is added, the product always consists of a mixture of the tetrabromo- and *sym.*-dibromo-derivatives. We were unable to isolate the tribromohydrindone from the products

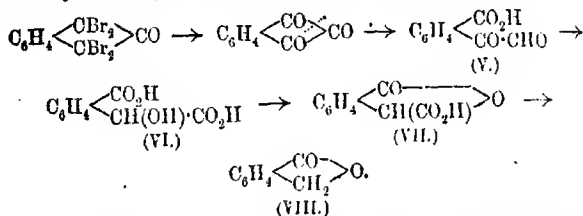
of this reaction, and it is apparently not formed under the experimental conditions employed.

There is no doubt that the monobromo-, dibromo-, and tetrabromo-derivatives of β -hydrindone prepared in this way have the formulæ

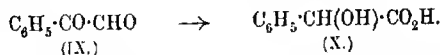


respectively. This is shown by the fact that they are all true ketones insoluble in alkalis. Moreover, the position of the bromine atoms in the hydrindene ring is proved by their behaviour towards hot aqueous potassium hydroxide, when products free from bromine are in each case obtained. Unfortunately, these products from the monobromo- and dibromo-derivatives are ill-defined, since internal condensation always ensues with the formation of compounds of high molecular weight, but the formation of phthalidecarboxylic acid (VII) from $\alpha\gamma$ -tetrabromo- β -hydrindone with this reagent clearly shows that the bromine atoms of all these bromine derivatives are in the hydrindene ring.

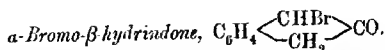
The curious formation of phthalidecarboxylic acid in this manner is evidently caused by the following series of reactions:



The conversion of a compound of formula (V) into a derivative of mandelic acid (VI) is quite analogous to the conversion of benzoyl formaldehyde (IX) into mandelic acid (X), which von Pechmann has shown (*Ber.*, 1887, 20, 2539) takes place readily in the presence of dilute alkali:



It is evident, therefore, that the phenomenon of inhibition does not arise when elements of high atomic weight are introduced. It is therefore probably a question entirely of molecular volume.



The preparation of β -hydrindone for the purposes of these experiments was effected by means of the reactions described previously

(Trans., 1908, 93, 186). 1.17 Grams of β -hydrindone were dissolved in well-dried chloroform and the solution mixed as quickly as possible with 3.2 c.c. of a solution of bromine in chloroform (1 c.c. = 0.4255 gram Br). A violent reaction ensued, and the colour of the bromine rapidly disappeared, leaving the solution pale yellow in colour; at the same time large quantities of hydrogen bromide were evolved. When the reaction was complete, the chloroform solution was slowly concentrated on the water-bath until the residue solidified on cooling, when the solid was spread on a porous plate until free from oil. α -Bromo- β -hydrindone may be recrystallised either from methyl alcohol or from light petroleum (b. p. 80—90°), and can be obtained from either solvent in colourless prisms melting at 91°:

0.1931 gave 0.1730 AgBr. Br = 38.1.

C_9H_7OBr requires Br = 37.9 per cent.

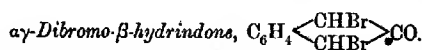
α -Bromo- β -hydrindone is soluble in all the usual organic solvents, and is characterised by possessing greater solubility in methyl alcohol and in light petroleum than either the dibromo- or tetrabromo-derivatives. It is insoluble in cold aqueous alkali hydroxides or carbonates, but rapidly darkens on boiling with these reagents, leaving ultimately a black solid free from bromine from which, however, no definite products could be isolated. When boiled with water, the hydrindone loses, hydrogen bromide, and slowly passes into solution, from which, on cooling, a viscous oil separates not containing bromine. Up to the present, we have not succeeded in obtaining this oil in a solid condition.

Conversion of α -Bromo- β -hydrindone into α -Cyano- β -hydrindone.—This conversion was carried out in order to prove that the bromine atom of α -bromo- β -hydrindone is in the hydrindene ring and not in the benzene nucleus. Five grams of the bromo-derivative were dissolved in alcohol and mixed with a concentrated aqueous solution of excess of potassium cyanide, the operation being carried out in a flask fitted with a reflux condenser, so arranged that a current of hydrogen could be passed by means of a narrow tube down the condenser and thus replace all the air in the flask throughout the reaction. This precaution was found to be necessary since both α -bromo- β -hydrindone and α -cyano- β -hydrindone rapidly oxidise in the presence of alkali. After the contents of the flask had been heated on the water-bath for two hours, they were filtered as rapidly as possible, and the filtrate acidified with dilute hydrochloric acid. The solid which then separated was collected and recrystallised from dilute alcohol, when the characteristic plates of α -cyano- β -hydrindone, melting and decomposing at 172°, were obtained (compare Trans., 1908, 93, 179):

0.2213 gave 17.1 c.c. N_2 at 18° and 764 mm. $N = 9.0$

$C_{10}H_7ON$ requires $N = 8.9$ per cent.

From this experiment it is therefore evident that the bromine atom in α -bromo- β -hydrindone is in the α -position of the hydrindene ring.



This substance was prepared in the same manner as the monobromo-derivative, 1.85 grams of β -hydrindone being dissolved in dry chloroform and mixed as rapidly as possible with 10.5 c.c. of a solution of bromine in chloroform (1 c.c. = 0.4255 gram Br). A vigorous reaction took place, and just as in the former case the whole of the bromine was quickly absorbed, considerable quantities of hydrogen bromide being at the same time eliminated. The pale yellow chloroform solution was then concentrated on the water-bath to a small bulk, when the residue solidified on cooling. The solid was spread on a porous plate and recrystallised, first from methyl alcohol and finally from light petroleum (b. p. $80-90^\circ$), being obtained in large, colourless needles melting at 111° . The compound becomes red on exposure to the air:

0.1963 gave 0.2555 AgBr. Br = 55.4.

$C_6H_6OBr_2$ requires Br = 55.2 per cent.

$\alpha\gamma$ -Dibromo- β -hydrindone is much less soluble in hot methyl alcohol and in hot light petroleum than α -bromo- β -hydrindone, and these two substances can be readily separated from one another by means of these solvents. It is insoluble in cold aqueous alkali hydroxides and in alkali carbonates, but when boiled with these reagents becomes first red and finally dark green. We were unable to isolate any definite products from this reaction, the dark green substance formed in the manner described above being insoluble in all the usual organic solvents, and therefore impossible to purify. It does not contain bromine.

$\alpha\alpha\gamma$ -Tribromo- β -hydrindone.

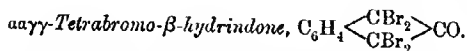
It has already been mentioned that in the experiment which should have yielded this tribromo-derivative a mixture of the dibromo- and tetrahydro-derivatives was obtained, but although the experiment in this respect was unsuccessful, yet it is worthy of recording because the mixture of the two bromo-compounds behaves in many respects as a homogeneous substance having the composition of the tribromo-derivative, and for some time we did not recognise that it was in reality a mixture. The bromination was effected in the usual way, the exact quantity of the chloroform solution of bromine (for 6 atoms)

being added all at once to a weighed quantity of β -hydrindone dissolved in chloroform. The colour of the bromine did not immediately disappear, and it was found necessary to warm the chloroform solution in a flask fitted with a reflux condenser for some time before the whole of the halogen had been absorbed. It is evident, therefore, that the formation of the bromo-derivatives of β -hydrindone at the ordinary temperature ceases with the dibromide, and that beyond this the aid of heat is required. After all the bromine had been absorbed, the chloroform solution was evaporated, the solid residue spread on a plate and finally recrystallised from methyl alcohol. In this way colourless prisms were obtained which appeared to be quite homogeneous and which melted fairly sharply at 153° ;

0.2135 gave 0.3274 AgBr. Br = 65.25.

$C_6H_8OBr_4$ requires Br = 65.0 per cent.

The analysis therefore agrees closely with $\alpha\alpha\gamma$ -tribromo- β -hydrindone, and we saw no reason to doubt the homogeneous character of this substance until while recrystallising a quantity of it from light petroleum (b. p. $80-90^{\circ}$) we noticed that a portion appeared to be much less soluble in this solvent than the remainder. Ultimately it was found that by repeated fractional recrystallisation from light petroleum two substances could be isolated, one of which melted at 111° and the other at 173° . Direct comparison proved the former to be $\alpha\gamma$ -dibromo- β -hydrindone and the latter to be $\alpha\alpha\gamma\gamma$ -tetrabromo- β -hydrindone. It is probable, although we have not experimentally investigated the point, that $\alpha\gamma$ -dibromo- β -hydrindone and $\alpha\alpha\gamma\gamma$ -tetrabromo- β -hydrindone are isomorphous, and that the substance melting at 153° is an isomorphous mixture of molecular proportions of the two. It is unusual, however, for an isomorphous mixture to possess so definite a melting point, but any further doubts on this point were set at rest by recrystallising a prepared mixture of the two constituents from methyl alcohol, when the substance melting at 153° was again obtained.



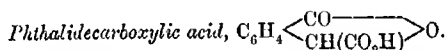
In order to prepare this substance, 3 grams of β -hydrindone were dissolved in dry chloroform and mixed with 34.4 c.c. of a solution of bromine in chloroform (1 c.c. = 0.4255 gram Br), the whole being subsequently placed in a flask fitted with a reflux condenser and heated on the water-bath for two hours. At the end of this time the colour of the halogen had completely disappeared, but in order to replace any possible loss of bromine which might have occurred during the process of heating, a further quantity (1.5 c.c.) of the chloroform solution of bromine was added and the heating continued

for half an hour longer. At the end of this time the chloroform solution, still slightly coloured by excess of bromine, was evaporated, and the solid which remained, after being spread on a porous plate, recrystallised from chloroform, or, better, from a mixture of chloroform and light petroleum (b. p. 80—90°). In this way the compound was obtained in large, colourless, rhombic prisms melting at 173°.

0.2009 gave 0.3370 AgBr. Br = 71.54.

$C_9H_4OBr_4$ requires Br = 71.4 per cent.

aa-Tetrabromo- β -hydrindone is very sparingly soluble in methyl alcohol and in light petroleum (b. p. 80—90°), and it can readily be separated from lower brominated products by means of either of these solvents. It is quite unacted on by cold alkali hydroxides, but gradually passes into solution on boiling, yielding ultimately phthalidecarboxylic acid.



This substance can be readily and quantitatively prepared from *aa*-tetrabromo- β -hydrindone by the action of hot potassium hydroxide solution. The finely-ground bromo-derivative is mixed with excess of a 20 per cent. solution of potassium hydroxide and boiled until all has passed into solution. During this process the bromide gradually dissolves, and when five grams are used the operation is usually finished at the end of one hour. The alkaline solution is then acidified with hydrochloric acid and extracted thoroughly with ether, the ethereal extract being subsequently shaken with dilute sodium carbonate solution. The sodium carbonate extract, after being acidified, is again extracted with ether, the ethereal extract being dried and evaporated. The residue, which solidifies on cooling, is then recrystallised from water, when colourless needles are obtained melting at 152°, and evolving carbon dioxide at about 180°:

0.1864 gave 0.4142 CO_2 and 0.0572 H_2O . C = 60.61; H = 3.41.

$C_8H_4O_4$ requires C = 60.7; H = 3.3 per cent.

The silver salt is precipitated as a white crystalline powder on adding a solution containing the calculated quantity of silver nitrate to a neutral solution of the ammonium salt:

0.3185 gave 0.1205 Ag. Ag = 37.83.

$C_8H_4O_4\text{Ag}$ requires Ag = 37.9 per cent.

The acid when distilled yielded an oily distillate, which solidified on cooling. On recrystallising the distillate from water, colourless needles were obtained melting at 73°:

0.1795 gave 0.4701 CO_2 and 0.0746 H_2O . $\text{C} = 71.42$; $\text{H} = 4.61$.

$\text{C}_8\text{H}_6\text{O}_2$ requires $\text{C} = 71.6$; $\text{H} = 4.5$ per cent.

The compound is therefore phthalide, and the acid, phthalide carboxylic acid.

MANCHESTER UNIVERSITY.

CXLVI.—*The Constituents of Canadian Hemp.* *Part I. Apocynin.*

By HORACE FINNEMORE, B.Sc.

THE root of Canadian hemp (*Apocynum cannabinum*) has the useful property of retarding the heart in systole, and is employed as a remedy for dropsy and heart troubles; it is official in the United States. Although Husemann pointed out, in 1876, that the medicinal value of the drug was probably due to the presence of a constituent analogous to digitalin, it does not appear to have been examined closely until 1883, when Schmiedeberg (*Arch. Exp. Path. Pharm.*, 16, 161) obtained from it two substances, which he named apocynin and apocynin respectively. The first of these had the characteristic physiological properties of *Apocynum*, but as the product appeared to be amorphous and resinous, and was obtained, moreover, only in very small quantity, it was not examined chemically.

The so-called apocynin of American pharmacy is merely the product obtained by precipitating the alcoholic extract with water and subsequently drying, but a definite crystalline substance is now produced commercially in small quantities under the same name, and has also been isolated by Wood (*J. Amer. Med. Assoc.*, 1904, 43, 1953) from the alcoholic extract. Wood's apocynin was considered by him to be identical with the crystalline commercial product, and melted at 113° ; no analysis was made, however, and pharmacological examination seemed to render it doubtful whether it was the active constituent sought. Inquiry having recently arisen as to the cause of certain untoward symptoms following the use of this drug, it was decided to re-investigate the nature of its active constituents on an adequate scale.

Isolation of Apocynin.

Forty kilos. of commercial *Apocynum cannabinum* root,* reduced to a coarse powder, were exhausted with hot 90 per cent. alcohol, for

* The cost of this large quantity of material was defrayed from the grant made by the Royal Society to the Physiological Department of Guy's Hospital, for which the author desires to express his thanks.

which purpose a copper Soxhlet apparatus was constructed capable of taking a charge of about 4 kilos. of the drug. Subsequent extraction of the residues with water yielded nothing further. The greater part of the alcohol having been removed by distillation, the remainder was expelled by heating with water in an open vessel. On cooling the aqueous solution thus obtained, a dark brown, resinous mass was deposited, which, after being twice extracted with boiling water, was reserved for subsequent examination. The united aqueous solutions were then extracted many times with ether, the aqueous residue again being reserved for further examination.

The combined ethereal extracts yielded on removal of the solvent a comparatively large amount of a pale brown, syrupy residue, which speedily deposited a copious, crystalline product. After recrystallisation from ether at the ordinary temperature, and further recrystallisation from dilute alcohol or hot water, this proved to be a well-defined substance identical with the crystalline apocynin of commerce. In all about 80 grams of this compound were obtained, representing a yield of 0.2 per cent. on the original material. Both the resin deposited from the alcoholic extract on treatment with water, and the residue of the aqueous solution after extraction with ether, yielded other equally definite products, although in smaller quantities; these are still under investigation, the results of which it is hoped to communicate later.

Apocynin crystallises in slender, colourless prisms, melts sharply at 115° (corr.), and may be distilled at about 300° without undergoing serious decomposition. It has a faint odour recalling that of vanillin. Although it may be sublimed slowly on a water-bath, apocynin is comparatively slightly volatile with steam; it is readily soluble in hot water, alcohol, ether, or chloroform, sparingly in cold water, and practically insoluble in light petroleum, by which it may conveniently be precipitated from alcoholic solution. There is no doubt as to its identity with the products already mentioned: the crystalline appearance is similar to that depicted photographically by Wood; the melting point is the same as that of the crystalline apocynin of commerce, and is unaffected by admixture with this substance. Further, the characteristic derivatives (page 1518) are identical:

- I. 0.1947 gave 0.4629 CO_2 and 0.1074 H_2O . $\text{C} = 64.8$; $\text{H} = 6.1$.
- II. 0.2480 „ 0.3531 CO_2 „ 0.0816 H_2O . $\text{C} = 65.1$; $\text{H} = 6.1$.
- 0.2051 in 19.65 acetic acid gave a depression of 0.23° . $\text{M. W.} = 175$.
- 0.4589 „ 19.65 „ „ „ 0.52° . $\text{M. W.} = 173$.
- $\text{C}_9\text{H}_{10}\text{O}_3$ requires $\text{C} = 65.1$; $\text{H} = 6.0$ per cent. $\text{M. W.} = 166$.

Phenolic Derivatives of Apocynin.

Apocynin gives the usual phenolic reactions. It is soluble in cold alkalis, from which it is precipitated unchanged by carbon dioxide or dilute acids. It is particularly characterised by the formation of a deep bluish-violet coloration with ferric chloride in aqueous solution, which disappears on boiling with excess of the reagent, owing to the formation of an insoluble product.

The *potassium* derivative was prepared by the addition of the calculated amount of alcoholic potassium hydroxide to an alcoholic solution of apocynin (1.66 gram) at the ordinary temperature, and in the course of twenty-four hours was deposited as a crystalline mass. After recrystallisation from a mixture of moist ethyl and amyl alcohols, it formed well-defined, colourless needles. It is an unstable compound, however, and, after being kept for some weeks, was no longer soluble in alcohol:

0.4080 gave 0.1540 K_2SO_4 . $K = 16.9$.

$C_9H_9O_3K, 1\frac{1}{2}H_2O$ requires $K = 16.9$ per cent.

The *acetyl* derivative was obtained by heating apocynin (2 grams) with acetic anhydride (10 grams) and dry sodium acetate (2 grams) in a reflux apparatus for four hours. After shaking the clear product with water, a crystalline substance slowly separated, which, after recrystallisation from dilute alcohol, formed colourless needles and melted at 57° (corr.):

0.1401 gave 0.3125 CO_2 and 0.0742 H_2O . $C = 60.8$; $H = 5.8$.

$C_{11}H_{12}O_4$ requires $C = 60.8$; $H = 5.8$ per cent.

The *benzoyl* derivative was prepared by shaking apocynin (1 gram) with benzoyl chloride and aqueous sodium hydroxide. The solid product, when washed with water and recrystallised from dilute alcohol, was obtained in silky, needle-shaped crystals melting at 106° (corr.). This derivative is especially well adapted for the identification of apocynin, as the crystals are particularly beautiful and characteristic:

0.1695 gave 0.4405 CO_2 and 0.0829 H_2O . $C = 70.9$; $H = 5.4$.

$C_{16}H_{14}O_4$ requires $C = 71.1$; $H = 5.2$ per cent.

An identical product was made from crystalline commercial apocynin.

The *methyl-ether* was prepared by adding sodium (0.6 gram) to a solution of apocynin (4 grams) and methyl iodide (4 grams) in methyl alcohol. After boiling in a reflux apparatus on a water-bath for two hours, the alcohol was distilled off and the residue poured into water. On extracting the whole with ether and removing the solvent from the dried solution, an oil was obtained which soon crystallised. After recrystallisation from dilute alcohol, it formed colourless, nearly rectangular prisms, and melted at 51° (corr.):

0.1568 gave 0.3825 CO_2 and 0.0955 H_2O . $\text{C} = 66.5$; $\text{H} = 6.7$.

$\text{C}_{10}\text{H}_{12}\text{O}_3$ requires $\text{C} = 66.6$; $\text{H} = 6.6$ per cent.

This compound is insoluble in alkalis, and does not give the phenolic reactions described above.

Presence of a Methoxyl Group in Apocynin.

Three determinations by the Zeisel-Perkin method gave results indicating the presence of a single methoxyl group; these, however, although concordant, were somewhat low (17.0, 17.0, 17.2 per cent.). On repeating the estimation with the addition of acetic anhydride, as recommended by Hewitt and Moore (Trans., 1902, 81, 318), the following result was obtained:

0.3471 gave 0.4929 AgI. $\text{OMe} = 18.7$.

$\text{C}_8\text{H}_7\text{O}_2 \cdot \text{OMe}$ requires $\text{OMe} = 18.7$ per cent.

On extracting the residuo with ether, after the estimation a small quantity of a crystalline substance was obtained, giving a green colour with ferric chloride, which changed to purple on the addition of sodium carbonate, the characteristic reaction of catechol derivatives. Apocynin is itself characterised by forming a bright red colour when boiled with 50 per cent. sulphuric acid, accompanied by the liberation of a volatile product closely resembling guaiacol in odour.

Ketonic Derivatives of Apocynin.

Although apocynin, like most phenols, readily reduces ammoniacal silver nitrate, it is without action on alkaline copper solutions, and does not restore the colour to leuco-magenta. The third oxygen atom is therefore not aldehydic; its ketonic character, however, is established by the formation of an oxime, a hydrizone, and a semicarbazone.

The oxime was prepared by dissolving apocynin (1 gram) in 90 per cent. alcohol (2 c.c.), diluted with water (10 c.c.), and then adding hydroxylamine hydrochloride (1 gram) and crystallised sodium carbonate (2 grams). After heating the whole on a water-bath for forty-five minutes, the product, from which an oil had separated, was poured into water and extracted with ether. The ethereal extract was washed and dried and the solvent removed, when the oxime was obtained as an oil, which only crystallised after keeping for some days in a vacuum desiccator. It formed groups of radiating prisms, and melted about $80-90^\circ$. As the yield of this product was very poor and the amount of material limited, it was not thought necessary, in view of the very well-defined character of the phenylhydrazone and the semicarbazone, to prepare a further quantity for analysis.

The phenylhydrazone was obtained by heating apocynin (1.66 gram)

in aqueous alcoholic solution (10 c.c. of alcohol and 20 c.c. of water) with phenylhydrazine hydrochloride (1.44 grams in 10 c.c. of water) and crystallised sodium acetate (1 gram) on a water-bath for an hour, when a brown oil had separated, together with a few slender crystals. On dissolving this product in alcohol and reprecipitating with water, it soon solidified. After recrystallisation from alcohol, the hydrazone formed flat, yellow needles, becoming reddish-brown after some time, and melting at 126° (corr.):

* 0.1515 gave 14.7 c.c. N_2 at 26° and 764 mm. $N = 11.2$.

$C_{15}H_{16}O_2N_2$ requires $N = 10.9$ per cent.

The semicarbazone was prepared by adding a solution of semicarbazide hydrochloride (2 grams) and crystalline sodium acetate (2 grams) in water (5 c.c.) to a solution of apocynin (2 grams) in 50 per cent. alcohol (20 c.c.). After three hours, crystals deposited, which, after recrystallisation from dilute alcohol, formed colourless needle-shaped prisms, and melted at 166° (corr.):

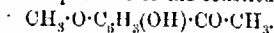
0.2180 gave 35.0 c.c. N_2 at 28° and 764 mm. $N = 18.4$.

$C_{10}H_{13}O_3N_3$ requires $N = 18.8$ per cent.

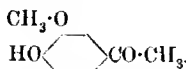
* An identical product was obtained from crystalline commercial apocynin.

Constitution of Apocynin. Identity with Acetovanillone.

The above results not only account for the whole of the oxygen in the apocynin molecule, but also practically establish its constitution, except as regards the orientation of the groups. A phenolic ketone of the formula $C_9H_9O_3$, containing a methoxyl group, cannot be other than a derivative of acetophenone of the constitution



The fact that the diphenol obtained in the course of the methoxyl determination shows the colour reaction characteristic of catechol, and that the substance itself when heated with sulphuric acid gives the colour of guaiacol, indicates with considerable probability that it is a derivative of the latter. The resemblance of the odour of the substance, albeit faint, to that of vanillin (4-hydroxy-3-methoxybenzaldehyde) also suggests very strongly that it is the methyl ketone corresponding with this compound, and having therefore the constitution represented by the formula:



This conclusion was entirely confirmed. Apocynin is identical with the acetovanillone which was isolated by Tienmann (*Ber.*, 1892, 24, 2855) in small quantity from a resinous by-product of the oxidation of

isoeugenol, and subsequently obtained by Goldschmiedt and Hemmelmayr (*Monatsh.*, 1904, 35, 338) by the hydrolysis of scoparin. The substances and their derivatives so completely correspond in composition and properties that further work in this direction was superfluous.

The melting points of the various products are given in the following table. The first and second columns give those obtained by the author in the course of the present investigation; the third and fourth give those obtained by Neitzel and by Goldschmiedt from acetovanillone prepared from isoeugenol and scoparin respectively; in the fifth are added the melting points of apocynin and its derivatives as prepared synthetically by the present author (see following paper).

	Apocynin, crystalline commercial.	Apocynin, natural. (Finne- more).	Acetovanillone.		Apocynin, synthetic (Finne- more).
			from isoeugenol. (Neitzel).	from scoparin. (Gold- schmiedt).	
Ketone	115°	115°	115°	115°	115°
Acetyl derivative ...	—	57	58	57—58	—
Benzoyl „	106	106	106	—	106
Methyl ether.....	—	51	48—49	—	—
Oxime	—	80—90	95	—	—
Phenyldiazone.....	—	126	126	125	128
Semicarbazone.....	166	166	—	—	166

Otto's and Neitzel's Syntheses of Acetovanillone.

The constitution of acetovanillone was determined by Tiemann from the above and other experimental data of Neitzel, the orientation of the groups being conclusively established by the oxidation of the acetyl compound to vanillic acid and of the methyl ether to veratric acid. The identity with 4-hydroxy-3-methoxyacetophenone was further confirmed by two syntheses of acetovanillone. Neitzel (*loc. cit.*) describes its production, although only in minute quantity, by distilling calcium vanillate with calcium acetate. Otto (*Ber.*, 1891, 24, 2869), also working in Tiemann's laboratory, describes its synthesis, in amount sufficient for analysis, by the condensing action of aluminium chloride and zinc chloride on a solution of guaiacol in acetic acid.

As it was desirable to obtain a synthetic specimen of apocynin, in order to compare its physiological properties with those of the natural product, the synthetic experiments of Neitzel and of Otto on acetovanillone were repeated. The results, however, were unsatisfactory, and it was found impracticable to form sufficient material for detailed examination.

Distillation of calcium vanillate with calcium acetate according to Neitzel's directions yielded mainly acetone, the only crystalline product

obtained being a few milligrams of a substance melting about 98° , which gave the characteristic colour reactions of catechol (m. p. 104°). A repetition of the dry distillation under the more favourable conditions afforded by conducting the operation under reduced pressure in an atmosphere of carbon dioxide and with the aid of a bath of fusible metal, gave a minute amount of a crystalline product which may have been acetovanillone, but it is impossible to say definitely. Neitzel himself, indeed, does not even give the melting point of his product, but merely states that "Das so hergestellte Präparat zeigte alle Eigenschaften des Acetovanillons."

Otto's method proved less unsatisfactory, but the yield was too small for any practical purpose. From 60 grams of guaiacol, following the directions of this worker, 0.6 gram of crude, dark-coloured acetovanillone and 0.4 gram of fairly pure substance was obtained. This was still somewhat coloured, however, and melted indefinitely at $96-109^{\circ}$, but it gave the colour reactions of apocynin and yielded the characteristic benzoyl derivative, melting at 106° . In the light of Gattermann's later observation (*Ber.*, 1892, 25, 3232) that guaiacol is readily converted into catechol by the action of aluminium chloride, it is now difficult to see how Otto's method could afford any notable yield of the condensation product he sought.

The physiological properties of apocynin and the other substances which the author has isolated from *Apocynum cannabinum*, and of the compounds which have been produced incidentally, are in course of determination by Mr. P. P. Laidlaw, M.B., in the Physiological Laboratory of this Hospital, and communication of the results is deferred until the work is completed.

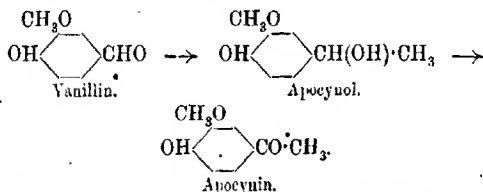
The author desires to express his thanks to Dr. Wade for the interest he has taken in this investigation, and the advice he has given throughout its progress. Acknowledgment is also due to Dr. F. B. Power for his courtesy in suspending the investigation of *Apocynum*, which had been commenced in his laboratory, on hearing that the author was already engaged on the same problem.

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CXLVII.—*A New Synthesis of Apocynin.*

By HORACE FINNEMORE, B.Sc.

IN view of the inadequacy of the methods already available for the synthesis of acetovanillone, with which the author has shown apocynin to be identical (preceding paper), and the desirability of obtaining apocynin for pharmacological, and perhaps medicinal, purposes by a less tedious and expensive method than that involved in its extraction from Canadian hemp (*ibid.*), new syntheses were sought. Apocynin is the methyl ketone corresponding with the aldehyde vanillin, and, at Dr. Wade's suggestion, it was decided to attempt a synthesis from this aldehyde by an application of the Grignard reaction. The aldehyde, it was thought, might be converted by magnesium methyl iodide into the corresponding methyl carbinol, which would conveniently be termed *apocynol*, and this, on oxidation, might yield the methyl ketone sought.



Although phenolic hydroxyl is known to react readily with the Grignard reagent, it was thought that the aldehyde group might perhaps be attacked preferentially if the calculated amount of material were employed, and that the additional operations involved in protecting the phenolic hydroxyl during the synthesis might thus be avoided. Some preliminary experiments with vanillin showed, however, that this was not so. There was in every case an immediate reaction with magnesium methyl iodide in ethereal solution and a copious precipitation of a solid product, but on working this up in the usual manner a large proportion of the vanillin was recovered unchanged, and it is doubtful whether any of the expected carbinol was formed.

On repeating the experiment with benzoylated vanillin, however, a good yield of the benzoylated carbinol was at once obtained. This product, moreover, proved to have the additional advantage of ready convertibility into the benzoylated ketone, from which synthetic apocynin could be isolated in satisfactory quantities. The following scheme shows the various compounds isolated in the course of this synthesis and the connexions established between them. The benzoyl-vanillin was prepared in the usual manner from pure commercial

Benzoylvanillin (m. p. 76°) → Benzoylapocynol (m. p. 123°) → Benzoylapocynin (m. p. 105°)
 ↓
 Vanillin (m. p. 82°) → Apocynol (m. p. 101°) → Apocynin (m. p. 115°)

A solution of carefully dried benzoylvanillin (25.6 grams) in ether which had been dried successively with sodium and phosphoric oxide was poured with constant shaking into a reflux apparatus containing a freshly prepared solution of magnesium methyl iodide prepared in the usual manner (dried magnesium turnings, 2.4 grams; freshly distilled methyl iodide, 14.2 grams; dry ether, 80 c.c.). There was an immediate precipitation of a solid product, which at first redissolved on shaking with development of heat; when, however, about one-third of the benzoylvanillin solution had been added, the precipitate ceased to redissolve, and the reaction proceeded more quietly. After boiling for half an hour on a water-bath in order to ensure completion, the well-cooled product was decomposed by adding ice in small pieces, followed by excess of dilute sulphuric acid.

The clear liquid which was thus obtained separated into an aqueous and an ethereal layer; the aqueous layer was separated and extracted twice with ether, the ethereal extracts being added to the original ethereal solution. The combined ethereal solutions were dried over anhydrous sodium sulphate, and on removing the solvent a clear amber-coloured oil was obtained, which, when dissolved in absolute alcohol (15 c.c.), quickly solidified to a crystalline mass. It was recrystallised from the same solvent. The average yield with these quantities was 23 grams, or 85 per cent. of the theoretical.

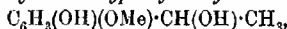
Benzoylapocynol, $C_6H_5(Obz)(OMe) \cdot CH(OH) \cdot CH_3$, forms small, colourless, rhombic prisms, and melts at 128° (corr.):

0.2171 gave 0.5591 CO_2 and 0.1175 H_2O . $\text{C} = 70.2$; $\text{H} = 6.0$.
 $\text{C}_{16}\text{H}_{16}\text{O}_4$ requires $\text{C} = 70.6$; $\text{H} = 5.9$ per cent.

Isolation of Apocynol.

On boiling benzoylapocynol (8.3 grams) with dilute aqueous potassium hydroxide (3 grams in 120 c.c. of water) in a reflux apparatus, it gradually dissolved, and, after twenty minutes, a clear solution was obtained. After boiling for ten minutes longer, the solution was cooled and saturated with carbon dioxide. A small amount of resinous matter having been filtered off, the solution was extracted with ether. The ethereal solution was dried with anhydrous sodium sulphate, and on removing the solvent an oil was obtained, which crystallised in the course of a few hours.

Apocynol (4-hydroxy-3-methoxyphenylmethylcarbinol),



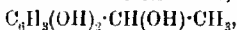
has a distinct odour of cloves; it separates from alcohol in exceedingly well-defined, colourless, rhombic plates, and melts at 101° (corr.). Apocynol is fairly soluble in water and freely in alkalis; its aqueous solution gives a pure blue coloration with ferric chloride, which is unchanged by sodium carbonate:

0.1293 gave 0.3037 CO_2 and 0.0831 H_2O . $\text{C} = 64.1$; $\text{H} = 7.1$.

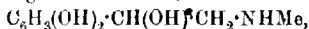
$\text{C}_9\text{H}_{12}\text{O}_3$ requires $\text{C} = 64.3$; $\text{H} = 7.1$ per cent.

A small amount of apocynol was also obtained by reducing natural apocynin with sodium amalgam in dilute alcoholic solution; the main product was a hard, crystalline substance melting at 185 – 190° , presumably a pinacone; this was not examined further, but a small quantity of oil was isolated, which had the odour of synthetic apocynol and gave the characteristic pure blue colour with ferric chloride.

When boiled with hydriodic acid as for a methoxyl determination, apocynol is converted into a catechol derivative,



which it is interesting to note differs from adrenaline,



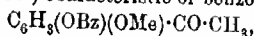
only by the absence of the terminal methylamino-group. This product is still under investigation; its physiological properties promise to be of interest, as do those of apocynol itself.

Conversion of Benzoylapocynol into Benzoylapocynin.

As already indicated, it was found impracticable to oxidise apocynol to the corresponding ketone, apocynin, without first protecting the phenolic hydroxyl group. Apocynol is oxidised readily enough by the ordinary agents, but apocynin itself is equally readily affected, so that

the oxidation products of the alcohol are complex. When, however, the phenolic hydroxyl is protected by benzylation, the ketonic group is comparatively stable towards mild oxidising agents, and the compound may be boiled with chromic acid mixture, for example, without serious loss. As benzoylapocynin is readily hydrolysed by dilute alkalis, this affords an easy method of obtaining apocynin from the initial product of the synthesis.

Benzoylapocynol (6.5 grams) was slowly added to a solution of potassium dichromate (10 grams) in 100 c.c. of water strongly acidified with sulphuric acid (10 grams). The mixture was constantly shaken, and the temperature slowly raised, the operation with these quantities lasting about thirty minutes. After boiling for two or three minutes to ensure the completion of the reaction, the product was cooled, and the hard cake of solid matter collected. This was washed several times with water and extracted in a reflux apparatus with 94 per cent. alcohol. On diluting the alcoholic solution with water, the beautiful silky needles (m. p. 106°) characteristic of benzoylapocynin,



p. 1515, were obtained.

The average yield of benzoylated ketone with the above quantities was 5 grams, or 77 per cent. of the theoretical :

0.1378 gave 0.3574 CO_2 and 0.0654 H_2O . C = 70.7 ; H = 5.2.

$\text{C}_{16}\text{H}_{14}\text{O}_4$ requires C = 71.1 ; H = 5.2 per cent.

Synthetic Apocynin.

The final stage in the synthesis of apocynin was effected by boiling synthetic benzoylapocynin (5 grams) with dilute sodium hydroxide (2 grams in 80 c.c. of water) in a reflux apparatus for twenty minutes. The substance rapidly dissolved, and, as the solution turned brownish-yellow in colour, the boiling was not further prolonged. Nothing separated on cooling the product, apocynin being freely soluble in alkalis, but on decomposing the sodium salt by saturating the solution with carbon dioxide, a portion of the ketone was precipitated in crystalline form ; the remainder was extracted with ether. The substance was still somewhat coloured, however, and required three crystallisations from hot water (the last with the addition of animal charcoal) before the colour was discharged. The yield was 1.7 grams, or 56 per cent. of the theoretical.

The synthetic apocynin thus obtained formed slender prisms identical with those of the natural product, and melted sharply at 115° (corr.), both alone and when mixed with natural apocynin. It possessed the faint odour of vanillin characteristic of the natural product, and gave the colour reactions already described (see preceding paper). On

benzoylation, it yielded the characteristic benzoyl derivative, melting at 106° ; with phenylhydrazine it gave the phenylhydrazone, melting at 126° , and with semicarbazide it yielded the semicarbazone, melting at 166° :

0.1900 gave 0.4523 CO_2 and 0.1066 H_2O . C = 64.9; H = 6.2.

$\text{C}_9\text{H}_{10}\text{O}_2$ requires C = 65.1; H = 6.0.

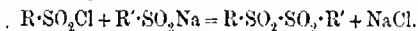
In conclusion, the author desires to express his thanks to Dr. Wade for the interest he has taken in this work, and for his constant advice during its progress.

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CXLVIII.—Aromatic α -Disulphones.

By THOMAS PERCY HILDITCH.

MANY instances might be given of well-known organic compounds containing at least two sulphone groups in the molecule, but until comparatively recently no method had been devised for the isolation of disulphones containing two sulphur atoms directly united to each other. About nine years ago, however, Kohler and MacDonald (*Amer. Chem. J.*, 1899, 22, 219) succeeded in preparing α -disulphones of this nature by the interaction of sulphonyl chlorides and the sodium salts of aromatic sulphonic acids, thus:



Dr. Smiles and the author (*Trans.*, 1907, 91, 519) observed that in the oxidation of *d*-camphor- β -sulphinic acid by potassium permanganate, about 12 to 18 per cent. (depending on the conditions of the reaction) was converted into *d*-camphoryl- α -disulphone.

The action of finely-powdered potassium permanganate in glacial acetic acid solution on several aromatic sulphonic acids has now been investigated, and it has been found that varying amounts of aromatic α -disulphones are always obtained in addition to the sulphinic acid which is invariably the main product. Relatively poor yields are obtained when the mixture is allowed to become warm or when the oxidation is performed in hot acetic acid, and the best method of carrying out the preparation is to add the calculated amount of finely-powdered permanganate in very small quantities at a time, the solution being constantly cooled and continuously shaken. The yield varied from about 17 per cent. in the case of *p*-xylenesulphinic acid to about

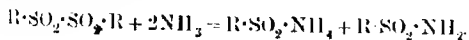
40 per cent. from *p*-toluenesulphinic acid, the smallest proportion being formed when an ortho-position with respect to the sulphonic nucleus was occupied by a methyl group.

The notable stability and other chemical properties of these compounds leave no doubt that they are disulphones, and, indeed, the manner in which they have now been obtained, taken in conjunction with Kohler and MacDonald's work, leads conclusively to the same formula. Thus there are two possible structures for the products from both methods of preparation, depending on whether the sulphinic acid reacts according to the formula $\text{R}\cdot\overset{\text{VI}}{\text{SO}}_2\text{H}$ or in the tautomeric form $\text{R}\cdot\overset{\text{IV}}{\text{SO}}\cdot\text{OH}$, as tabulated below:

Structure of acid.	Structure of product by method of	
	Kohler and MacDonald.	Hilditch.
$\text{R}\cdot\text{SO}_2\text{H}$	$\text{R}\cdot\text{SO}_2\cdot\text{SO}_2\cdot\text{R}$	$\text{R}\cdot\text{SO}_2\cdot\text{SO}_2\cdot\text{R}$
$\text{R}\cdot\text{SO}\cdot\text{OH}$	$\text{R}\cdot\text{SO}\cdot\text{O}\cdot\text{SO}_2\cdot\text{R}$	$\text{R}\cdot\text{SO}\cdot\text{O}\cdot\text{O}\cdot\text{SO}\cdot\text{R}$

Since the substances now obtained are identical with those prepared from the corresponding sulphinic and sulphonic acids by Kohler and MacDonald, it follows that they must be represented as α -disulphones, and that the sulphinic acids must be assumed to contain sexavalent sulphur. It may be asked whether the relative proportions of disulphone and sulphonic acid formed serve as any indication of the amounts of the two tautomeric forms of sulphinic acid present, but such a deduction does not seem valid, since, even although the form containing quadrivalent sulphur could hardly give rise to a disulphone on oxidation, there is no reason why a certain proportion of the other form should not yield sulphonic acid instead of disulphone.

The most notable physical characteristics of this group of compounds are well-defined, crystalline form, stability, sparing solubility in most solvents, and high melting point. Chemically they are somewhat inert; prolonged boiling with water resolves them very slightly into a mixture of free acids. They are not attacked by cold alkali hydroxides, but moderately concentrated and hot solutions of these reagents decompose them into a mixture of sulphonate and sulphinic acid, the former being recognised by conversion to the acid chloride, the latter by the melting point of the free acid and the deep blue coloration obtained by adding a drop of phenetole to the solution of the acid in cold concentrated sulphuric acid, which disappears on addition of excess of phenetole (Smiles and Le Rossignol, *Trans.*, 1906, **89**, 696). Similarly, with the strongest aqueous ammonia, these compounds are slowly converted on warming into a mixture of sulphonamide and sulphinic acid, thus:



Although Kohler and MacDonald state that these derivatives may be, "crystallised without loss from concentrated nitric acid," the author finds that on boiling with this reagent nitration ensues, the product consisting chiefly of a dinitro-substitution product.

EXPERIMENTAL.

Diphenyl- α -disulphone, $\text{C}_6\text{H}_5\cdot\text{SO}_2\cdot\text{SO}_2\cdot\text{C}_6\text{H}_5$.

Five grams of benzenesulphinic acid were oxidised in cold glacial acetic acid solution by 1 gram of finely-powdered potassium permanganate. After some hours, the mixture was poured into water and nearly neutralised with ammonia. About a gram of a white, insoluble product separated, which, when crystallised from boiling benzene, formed small, white needles melting at $193\text{--}194^\circ$. The substance is sparingly soluble in alcohol or cold benzene, and moderately so in hot benzene or glacial acetic acid. Hot concentrated ammonia led to the formation of benzenesulphonamide and ammonium benzenesulphinate; the latter was recognised by Smiles' test, and the former, after recrystallisation from alcohol, melted at $152\text{--}153^\circ$:

0.1093 gavo 0.2029 CO_2 and 0.0388 H_2O . $\text{C} = 50.64$; $\text{H} = 3.94$.

0.1461 ,, 0.2364 BaSO_4 . $\text{S} = 22.43$.

$\text{C}_{12}\text{H}_{10}\text{O}_4\text{S}_2$ requires $\text{C} = 51.06$; $\text{H} = 3.55$; $\text{S} = 22.70$ per cent.

Di- p -tolyl- α -disulphone, $\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_3$.

Two and a-half grams of crude product were obtained from the oxidation of 6 grams of p -toluenesulphinic acid in the manner described above. After recrystallising twice from benzene, small prisms, melting and decomposing at 221° (212° : Kohler and MacDonald, *loc. cit.*), were obtained:

0.1428 gave 0.2828 CO_2 and 0.0588 H_2O . $\text{C} = 54.0$; $\text{H} = 4.58$.

0.1682 ,, 0.2558 BaSO_4 . $\text{S} = 20.88$.

$\text{C}_{14}\text{H}_{14}\text{O}_4\text{S}_2$ requires $\text{C} = 54.20$; $\text{H} = 4.52$; $\text{S} = 20.64$ per cent.

By the action of hot ammonia, p -toluenesulphonamide, melting at 137° , and ammonium p -toluenesulphinate resulted; the substance dissolved slowly, but completely, in hot 50 per cent. aqueous potassium hydroxide, and, on acidifying with mineral acid and extraction with ether, crystals of p -toluenesulphinic acid were formed, melting at $85\text{--}86^\circ$. The aqueous residue on evaporation and treatment with phosphorus pentachloride yielded p -toluenesulphonyl chloride, melting at $66\text{--}68^\circ$.

Boiling nitric acid (sp. gr. 1.4) converted the substance almost completely into a very sparingly soluble compound containing nitrogen. The crude product consisted of cream-coloured needles, melting not

very sharply at $172\text{--}174^\circ$, and was exceedingly difficult to purify by reason of its insolubility. Analysis of the purest sample obtained indicated that a dinitro-derivative had been chiefly formed:

0.1308 gave 0.2066 CO_2 and $0.0488\text{ H}_2\text{O}$. $C = 43.06$; $H = 4.15$.

$\text{C}_{14}\text{H}_{12}\text{O}_8\text{N}_2\text{S}_2$ requires $C = 42.0$; $H = 3.0$ per cent.

Di-p-phenetyl- α -disulphone, $\text{C}_6\text{H}_5\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{C}_6\text{H}_5$.

Three grams of *p*-phenetylsulphinic acid, oxidised in glacial acetic acid by half a gram of potassium permanganate, yielded 1 gram of the disulphone, which crystallised in minute needles, and melted sharply at 208° , decomposing at the same time. It resembled the previous two compounds as regards solubility:

0.1958 gave 0.3710 CO_2 and $0.0912\text{ H}_2\text{O}$. $C = 51.68$; $H = 5.18$.

0.1600 „ 0.1980 BaSO_4 . $S = 16.99$.

$\text{C}_{18}\text{H}_{16}\text{O}_8\text{S}_2$ requires $C = 51.89$; $H = 4.86$; $S = 17.30$ per cent.

Di-p-xylyl- α -disulphone, $(\text{CH}_3)_2\text{C}_6\text{H}_3\cdot\text{SO}_2\cdot\text{SO}_2\cdot\text{C}_6\text{H}_3(\text{CH}_3)_2$.

The *p*-xylenesulphinic acid used was prepared by the sulphination of *p*-xylene with sulphur dioxide in presence of anhydrous aluminium chloride (Smiles and Le Rossignol, *Trans.*, 1908, 93, 745). By this process about 6 grams of pure sulphinic acid and 1—2 grams of *p*-xylene sulfoxide resulted from 10 grams of *p*-xylene. The sulphinic acid melted at 85° , and agreed in its properties with that obtained by Gattermann (*Ber.*, 1899, 32, 1144) from *p*-xyldine:

0.1109 gave 0.2287 CO_2 and $0.0580\text{ H}_2\text{O}$. $C = 56.26$; $H = 5.81$.

0.1955 „ 0.2700 BaSO_4 . $S = 18.97$.

$\text{C}_8\text{H}_{10}\text{O}_2\text{S}$ requires $C = 56.47$; $H = 5.88$; $S = 18.82$ per cent.

The sulfoxide was not closely examined.

The yield of α -disulphone obtained by oxidation in the usual way was about 17 per cent. The recrystallised product formed white needles, melting at 199° :

0.1612 gave 0.3348 CO_2 and $0.0799\text{ H}_2\text{O}$. $C = 56.65$; $H = 5.51$.

$\text{C}_{16}\text{H}_{18}\text{O}_4\text{S}_2$ requires $C = 56.80$; $H = 5.33$ per cent.

The author desires to express his thanks to Assistant-Professor Smiles for suggesting this research.

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CXLIX.—*On Polymorphism, with Especial Reference to Sodium Nitrate and Calcium Carbonate.*

By WILLIAM BARLOW and WILLIAM JACKSON POPE.

IN previous communications (Trans., 1906, 89, 1675; 1907, 91, 1150) the authors have submitted a considerable body of evidence indicating that the total volume occupied by a crystalline substance must be regarded as portioned out amongst the atoms of the component elements, consistently with the established homogeneity of crystal structure and the crystal form, according to the following two definite principles. 1. That the polyhedral space appropriated by each atom approximates to the spherical shape so far as the environing conditions will allow; this may be conveniently designated the principle of close-packing of spheres of atomic influence. 2. That the volume of the space which, in the case of any given compound, is thus allotted to an atom is approximately proportional to the fundamental valency of the element of which it consists; this may be called the law of valency volumes.

The tendency towards sphericity on the part of the atomic domain has been interpreted as arising from the establishment of equilibrium in the crystal structure of opposing attractive and repulsive forces operative between the component atoms of the molecule. It has been illustrated by constructing close-packed assemblages of spheres of deformable but incompressible material representing the arrangement of the atoms in the crystalline structures concerned, and supposing the assemblages subjected to a general compression from all sides, so as to flatten the spheres into polyhedra and to eliminate the interstitial space; a similar result is obtained by describing tangent planes at the points of contact between the spheres of the assemblage and regarding the spheres as exchanged for the polyhedra enclosed by the planes thus indicated. If, therefore, equilibrium of a structure obtains, it will be indicated by close-packing of the spheres employed to form the assemblage representing the structure; the volumes of polyhedra derived from the spheres, and constituting the spheres of influence of the component atoms, will be approximately proportional to the fundamental valencies of the elements concerned. The propriety of allotting or partitioning up the whole space among the atoms, without leaving interstices, becomes evident directly it is admitted that the atoms exercise individual influence according to some distance law. For every geometrical point within the structure must then be regarded as exposed to the paramount influence of some particular atom or atoms, and if the portion of space throughout which the influence

of a particular atom is paramount is allotted to this atom, the partitioning thus achieved necessarily excludes the presence of interstitial space. This consideration shows that the conception of interstitial space amongst the spheres of atomic influence composing the crystal structure is unnecessary.

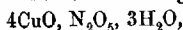
The results of the conclusions already put forward are obviously far-reaching and should be subjected to test in the light of phenomena other than those which have led inductively to their formulation. Tests of this kind have already been applied. Le Bas has demonstrated that in the normal paraffins the carbon atom appropriates a volume four times as great as that occupied by the hydrogen atom (*Trans.*, 1907, 91, 112; *Phil. Mag.*, 1907, [vi], 14, 324); Jaeger has shown that predictions as to crystalline form based upon the new theory are verified in practice (*Trans.*, 1908, 93, 317. Compare also Jerusalem and Pope, *Proc. Roy. Soc.*, 1908, 80 A, 557). Further light is thrown on the subject by, and substantial confirmation of the legitimacy of the methods employed results from, the study of the way in which the new conclusions apply to the crystalline forms of polymorphously related substances; the inquiry thus indicated is included within the scope of the present paper.

It has long been recognised that the polymorphously related forms of a substance are frequently related morphotropically (Pastern, *Ann. Chim. Phys.*, 1848, [iii], 23, 267), although the observed relationship is in general confined to a similarity between corresponding angles measured on the several modifications. Relationship of a far more intimate character should, however, exist, if the mode of treatment which we have adopted has any physical meaning. Thus, in accordance with the terminology which we have adopted, polymorphism may be defined as the existence of two or more close-packed assemblages, distinguished by difference of marshalling, all of which are partitionable into units or chemical molecules of practically identical configuration. The discussion of the relation existing between the cubic and the trigonal modifications of silver iodide (*Trans.*, 1907, 91, 1174) furnishes an illustration of this definition; both these materials are partitionable into molecular units of the same configuration.

The study of the case of silver iodide reveals a peculiarity to which is immediately traced the close morphotropic relationship between its cubic and trigonal forms, namely, that both modifications are to be regarded as built up from identical double layers as figured (*Trans.*, 1907, 91, 1174, Figs. 19 *a* and *b*). The occurrence of the two modifications of silver iodide is thus to be attributed to the possibility of close packing the same layers of spheres in accordance with either cubic or trigonal symmetry; the two crystalline modifications originate

in the different packing together of identical unit layers (*loc. cit.*, 1177). It is readily perceived that in all cases where two polymorphously related substances result from two different modes of close-packing of identical layers or sets of layers, it will be possible to convert the axial ratios descriptive of the one modification into those of the other by aid of some simple transposition; this has been already indicated in connection with the two modifications of silver iodide and of zinc sulphide (*loc. cit.*, 1178).

As other known instances in which a close relationship of similar kind occurs between polymorphously related substances, the following may be quoted. The orthorhombic mineral gerhardite,



which exhibits $a:b:c = 0.9217:1:1.1562$, is morphotropically almost identical with the synthetic substance, the latter being monosymmetric with $a:b:c = 0.9190:1:1.1402$, $\beta = 85^\circ 27'$ (Wells and Penfield, *Zeitsch. Kryst. Min.*, 1886, 11, 303). A similar approximate identity in axial ratios occurs between the two compounds of the composition $\text{NaGlHSi}_3\text{O}_8$; the monosymmetric mineral eudidymite has the axial ratios $a:b:c = 1.7107:1:1.1071$, $\beta = 86^\circ 14'$; whilst epididymite, having the same composition, is orthorhombic with the axial ratios $a:b:c = 1.7274:1:1.0680$. The double propionate of calcium and barium, $2\text{Ca}(\text{C}_8\text{H}_5\text{O}_2)_2, \text{Ba}(\text{C}_8\text{H}_5\text{O}_2)_2$, crystallises in the cubic system and forms two series of isomorphous mixtures, of cubic and tetragonal symmetry respectively, with the double propionate of calcium and lead, $2\text{Ca}(\text{C}_8\text{H}_5\text{O}_2)_2, \text{Pb}(\text{C}_8\text{H}_5\text{O}_2)_2$, which crystallises in the tetragonal system with $a:c = 1:0.9787$ (Fitz and Sansoni, *Zeitsch. Kryst. Min.*, 1882, 6, 68). It is obvious that the latter substance is pseudo-cubic, and that its equivalence parameters approximate very closely to those of the truly cubic calcium barium salt. Carbon tetrabromide, CBr_4 , is dimorphous, crystallising above 47° in the cubic system, and below that temperature in the monosymmetric system with $a:b:c = 1.7414:1:1.9617$, $\beta = 125^\circ 3'$ (Zirngiebl in *Groth, Chem. Kryst.*, 1906, 1, 231); as Groth has noted, the latter modification is pseudo-cubic, and if the observed forms $\{001\}$, $\{10\bar{1}\}$, and $\{110\}$ are assigned the indices $\{11\bar{1}\}$, $\{1\bar{1}1\}$, and $\{111\}$, and are referred to a set of anorthic axes, the axial ratios $a:b:c = 1.0260:1:1$, $\alpha = 89^\circ 44'$, β and $\gamma = 90^\circ 33'$, are obtained. The monosymmetric form is thus almost identical dimensionally with the cubic modification.

The hexagonal and orthorhombic modifications of silica are dimensionally related. Quartz, with $a:c = 1:1.0999$, may be referred to a set of orthorhombic axes, in which $b/a = \tan 60^\circ$, and the form $\{100\}$ is changed to $\{011\}$; the axial ratios then become $a:b:c = \cot 60^\circ:1:1.0999/\cos 30^\circ = 0.5774:1:1.2701$. In the orthorhombic mineral tridymite, with $a:b:c = 0.5774:1:0.9544$, the occurrence of

the forms {043} and {443} allows the latter indices to be changed to {111}; the axial ratios then become $a:b:c=0.5774:1:1.2716$. These values are almost identical with those calculated from the hexagonal modification of the substance. It has been pointed out by Beckenkamp (*Zeitsch. Kryst. Min.*, 1901, 34, 569) that quartz and tridymite can be referred to the orthorhombic parameters, $a:b:c=0.5774:1:0.9545$, and $0.5774:1:0.9544$, respectively.

The following instances, although of equal weight, are not so obvious as the foregoing, and, apparently for this reason, have not been previously remarked.

The accurate goniometric data furnished by Miers for the red silver ores (*Min. Mag.*, 1888, 8, 37; 1893, 10, 215) afford examples of polymorphous relationships very similar to, but even more striking than those existing between quartz and tridymite. The minerals of the composition, Ag_3SbS_3 , are the hemimorphously rhombohedral pyrrargyrite, with $a:c=1:0.7892$, and the monosymmetric fire blende, with $a:b:c=1.9465:1:1.0973$, $\beta=90^\circ$; the data for pyrrargyrite may be referred to a set of rectangular axes by transposing so that the forms {101} and {001} become respectively {011} and {010}. The axial ratios for the two minerals then become:

Pyrrargyrite	$a:b:c = 1.9007:1:1.0974$, $\beta = 90^\circ$
Fire blende	$a:b:c = 1.9465:1:1.0973$, $\beta = 90^\circ$.

On performing the same simple transposition with the axial ratio of the hemimorphously rhombohedral proustite, Ag_3AsS_3 , with $a:c=1:0.8039$, values are obtained which approximate to the axial ratios of the monosymmetric xanthoconite of the same composition, namely:—

Proustite	$a:b:c = 1.8671:1:1.0774$, $\beta = 90^\circ$.
Xanthoconite	$a:b:c = 1.9187:1:1.0152$, $\beta = 88^\circ 47'$.

The examples quoted above refer to cases in which two modifications of the same composition are sufficiently stable at the ordinary temperature to allow of goniometric measurement; it is, however, clear that dimensional correspondences such as those pointed out above should be also observed amongst cases of isopolymorphism. One illustration may be quoted in this connexion. Rubidium nitrate is pseudo-hexagonally orthorhombic with $a:b:c=1.7366:1:0.7108$ (Jaeger, *Zeitsch. Kryst. Min.*, 1907, 43, 588) and, owing to the equivalence of rubidium and sodium, should be isopolymorphously related to the rhombohedral sodium nitrate, which exhibits, $a:c=1:0.8276$. On referring the latter rhombohedral axial ratio to orthorhombic axes by transposing, so that

$$a:b:c = \tan 60^\circ : 1 : 0.8276 \cos 30^\circ = 1.7320 : 1 : 0.7151,$$

values almost identical with those for rubidium nitrate are obtained.

Thus:

Rubidium nitrate.....	$a:b:c = 1.7366:1:0.7106.$
Sodium nitrate.....	$a:b:c = 1.7320:1:0.7151.$

The numerous cases quoted above, in which the goniometric constants for two polymorphously related substances can be immediately referred to practically the same set of axial ratios, suggest the existence of a relation between the respective assemblages similar in character to that worked out for silver iodide. Stated in general terms, the conclusion must be drawn that where such dimensional coincidences obtain as between two polymorphously related assemblages, the latter are composed of practically identical layers or blocks of the aggregated spheres of atomic influence. It is, however, desirable to make the conclusion more obvious by constructing the assemblages representing some pair of polymorphously related substances, and for this purpose it is convenient to select the isopolymorphously related substances, sodium nitrate and potassium nitrate. The first of these is rhombohedral with $a:c = 1:0.8276$, and the latter orthorhombic with $a:b:c = 0.5910:1:0.7010$. The examination of these cases is the more important in that they are related by the second geometrical property to the two polymorphously related modifications of calcium carbonate (Trans., 1906, 89, 1732); the rhombohedral calcite shows $a:c = 1:0.8543$, and the orthorhombic aragonite exhibits $a:b:c = 0.6224:1:0.7206$. The whole method of treatment is subjected to a somewhat crucial test in being applied to these intimately related cases, and the more especially in that many data are available concerning the crystal structures of these well known substances.

In order to pave the way for this somewhat complicated investigation, it is convenient first to treat a case in which the assemblage is more easily derivable and which is closely related to that of sodium nitrate; for this reason the crystal structure of the tetartohedrally cubic barium nitrate is next discussed.

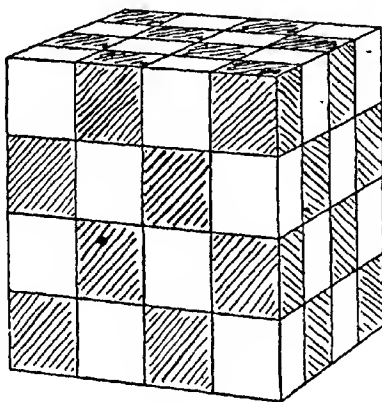
Barium Nitrate, Ba(NO₃)₂.

A close packed assemblage having the valency composition of the tetartohedrally cubic barium nitrate is related to a closest-packed assemblage consisting entirely of bivalent spheres of influence, of which three-fourths are oxygen, through the second geometrical property previously defined (Trans., 1907, 91, 1151 and 1201). If the remaining one-fourth of the spheres are removed from the assemblage and for each bivalent sphere abstracted, a sphere of volume three, representing a trivalent nitrogen atom, is substituted, additional

spheres have, according to the property referred to, to be inserted in the proportion of a valency volume unit for every substituted sphere, in order to produce close-packing without remarshalling in the altered assemblage. This requirement is met by adding a univalent sphere for every group $-\text{NO}_2$ or a bivalent sphere for every pair of such groups. A composition of the kind under consideration, namely, $\text{Ba}(\text{NO}_3)_2$, is thus attained.

When the cubic closest-packed arrangement of equal spheres is subjected to the above substitution, it appears that the most symmetrical method of selecting one-fourth of the spheres for replacement is one already described by the authors (Trans., 1907, 91, 1197, Fig. 30). The centres of the spheres thus selected for removal form

FIG. 1.

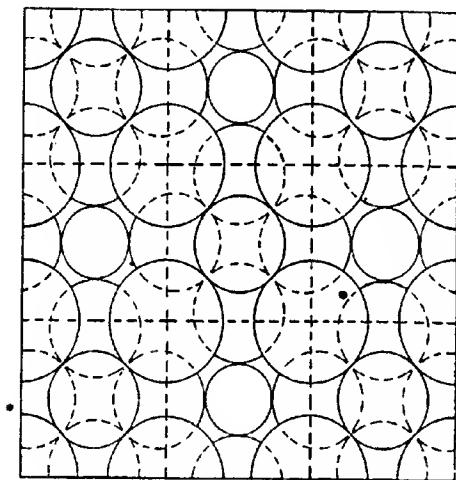


a cubic space-lattice, and the process of substitution can be carried out in harmony with cubic symmetry in the following manner.

The oxygen spheres remaining after the removal of one-fourth of the original number may be regarded as forming distinct octahedral groups of six so arranged that the centres of the groups are symmetrically situated at the centres of half the cubic cells outlined by joining the points of the cubic lattice formed by the centres of the removed spheres; since the centres of the spheres remaining are at the centres of the cube faces, either of the two sets of cubes in edge contact (Fig. 1), which together make up the entire number, can be selected as containing the centres of the octahedral groups (Trans., 1907, 91, 1170, Fig. 16). Let now the scale of the system of cube cells be increased uniformly while keeping the centres of the octa-

hedral groups of spheres at the centres of the selected half set of cubes; since each original block or unit of eight bivalent spheres, consisting of an octahedral group of six and the two which have been removed, is ultimately to be replaced by a unit representing the molecular composition $\text{Ba}(\text{NO}_3)_2$, the requisite increase of scale is given by the volume ratio of these two units, namely, $16 : 20 = 4 : 5$. The arrangement of the octahedral groups in a single layer of cells thus expanded is shown drawn to scale by the medium-sized circles of Fig. 2. • This diagram shows the projection of the contents of one set of alternate layers of cells; the projection of the other set on the same area would

FIG. 2.



be represented by a similar figure in which the two kinds of filling of the squares have changed places. The relation between the two projections is indicated by the non-continuous circles of Fig. 4, α and β .

In the system of cubic cells of Fig. 2, when containing only the octahedral groups of six bivalent spheres, two kinds of principal cavities are present, one at the centres of the set of cubes in edge contact not containing the group centres, the other, just twice as numerous, at all the cube angles. The latter cavities are of such a shape and size as accommodate spheres larger than those representing the trivalent nitrogen, and the cavities at the cube centres can similarly accommodate spheres smaller than those of a bivalent atom;

the positions and sizes of spheres such as fill the cavities are shown in projection in Fig. 2.

The assemblage thus completed, of which one layer is depicted in Fig. 2, has the composition indicated by $\text{Ba}(\text{NO}_3)_2$, if the small, the medium, and the large spheres respectively represent the spheres of atomic influence of barium, oxygen, and nitrogen; if constructed from incompressible, deformable spheres, and subjected to a general pressure, the equilibrium condition reached would show but little modification of the arrangement prevailing before the application of pressure, and would, just as before, display holohedral cubic symmetry. As, however, the small spheres used are much smaller than those of the bivalent size which should represent barium, and the large spheres are larger than those of the trivalent nitrogen size, it has to be ascertained what modification of the type of arrangement will occur when the spheres used are replaced by others representing barium, oxygen, and nitrogen, in accordance with the valency rule; the respective volumes of these spheres must be then approximately in the ratio 2:2:3.

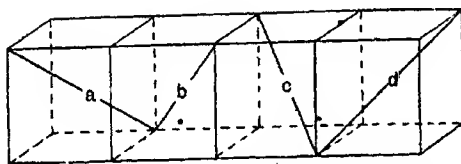
As the nitrogen spheres of volume three are too small to fill the cavities provided for them, it is evident that some relative movement of the octahedral groups of six oxygen spheres can occur without obstructing the introduction of nitrogen spheres of the proper magnitude; thus a certain slight symmetrical movement of the octahedral groups can take place which uniformly reduces the size of the nitrogen cavities so that each just suffices to contain a sphere of the correct volume three, and this movement is found to increase uniformly the magnitude of the cavities allotted to the barium spheres so that each will now accommodate a sphere of approximately the correct volume two. The symmetrical change thus involved is described below; whilst it results in the retention of cubic symmetry by the assemblage, it involves a degradation of the class of symmetry obtained to that of the tetartohedral cubic system to which barium nitrate belongs.

In the skeleton assemblage of octahedral groups of six oxygen spheres represented by the medium-sized circles of Fig. 2, one-fourth of the trigonal axes are selected as a set of non-intersecting trigonal axes having the relative positions already described (Trans., 1907, 91, 1183), the directions of these axes in their cells being indicated by the letters a, b, c, and d, on Fig. 3, according to the convention previously adopted. All the remaining trigonal axes are destroyed by a similar slight movement of each octahedral group, O_6 , along its selected trigonal axis; the displacement of any single group determines those of all the others, since they are derived from the first by the coincidence movements characterising the system of symmetry. The movements

of the original octahedral groups whose projections are given by the non-continuous circles of Fig. 4, *a* and *b*, are, both in direction and approximately in extent, expressed by the shift required to bring the continuous circles of the figure to coincidence with the non-continuous circles; the diagram represents the movement as a mere translation of each group along its trigonal axis in the appropriate selected direction without change of orientation, but a slight similar rotation of the octahedral groups about their trigonal axes accompanying the translation conduces towards the closeness of the final packing of the assemblage. This rotation component is not represented in the diagram in order to avoid complication; its introduction leads to no change of the type of symmetry.

The corners of the cells of the partitioning, having the same relative arrangement as that of the cell centres, are, like them, made up of two sets whose position relations are indicated by the two kinds of cubes previously distinguished in Fig. 1. Before the screw movements referred to occur, the cavities at the cell corners of both the

FIG. 3.

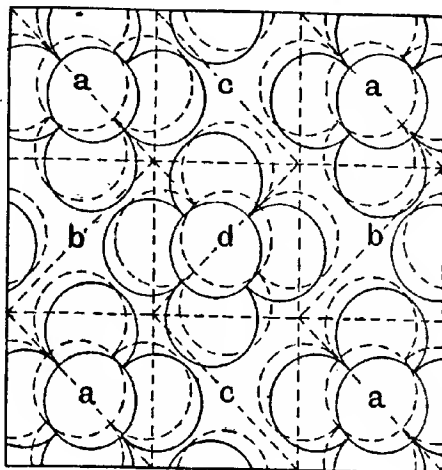


component sets are identical, and have identically the same relation to the assemblage of groups, but after the movements the two sets of cavities are distinguishable, for whilst those of each set are similarly changed, the change experienced by the cavities of one set differs from that experienced by those of the other set. The octahedral groups, O_6 , and the barium spheres are found to have approached the nitrogen spheres of one set along the common trigonal axis, and thus to have receded from the original places of the other set along this axis; these latter nitrogen spheres have, however, approached the barium spheres, and the total number of contacts is nearly the same for both sets of nitrogen spheres. The cavities at the cell corners for the accommodation of the barium spheres, which have been increased in size by the movement of the octahedral groups of oxygen spheres, remain identical with one another; all the spheres of the assemblage have experienced some shift from their original positions indicated in Fig. 2.

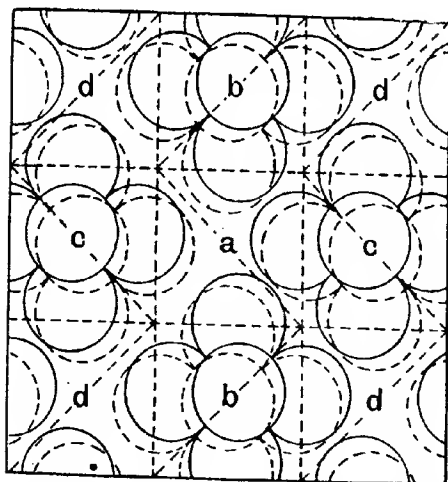
It is established by the foregoing that the assemblage of spheres of the magnitudes indicated by the valency relations of the elements

composing barium nitrate, $\text{Ba}(\text{NO}_3)_2$, is not in equilibrium in the holohedral cubic arrangement of the type shown in Fig. 2, and that, if

FIG. 4.



a.



b.

forced into an arrangement of this highly symmetrical type, it will, in seeking equilibrium, pass into some less symmetrical arrangement.

It is shown that passage to an equilibrium arrangement of the tetartohedral cubic type, numbered I in Barlow's list (*Zeitsch. Kryst. Min.*, 1894, 23, 1), can occur in the manner described above; the movements of the octahedral groups of oxygen spheres which lead to this equilibrium arrangement destroy all the elements of symmetry excepting those about a set of non-intersecting trigonal axes, and such other elements of symmetry as are involved in the existence of those axes.

When the equilibrium is pictured by an appropriately constituted assemblage of deformable spheres it is clear that, as in all other cases, the greatest flattening must occur of those spheres the actual contacts of which are relatively fewest, since the pressure on these spheres will be concentrated at a relatively small number of points on their surfaces. In harmony with this, the barium spheres, which have but six actual contacts each, must be more flattened than the others; the effect of this, like that of the movements, is to make a larger size of sphere available for the purpose without endangering the equilibrium.

The twinning of barium nitrate crystals, which occurs on {111}, does not appear to call for special remark, as it is traceable to the same kind of symmetrical disposition about a layer perpendicular to a trigonal axis as produces twinning in the case of the root assemblage to which the structure has just been referred (compare *Trans.*, 1907, 91, 1187). Consequently, if the root assemblage is twinned before the change is made in accordance with the second geometrical property, an equilibrium arrangement of the barium nitrate spheres of influence, which is derived from this twinned assemblage of equal spheres, will be that appropriate to the twinned form of the crystalline substance.

The above discussion of the crystal structure of barium nitrate naturally also holds for the other tetartohedrally cubic nitrates of the bivalent metals, namely, strontium and lead nitrates. The case has been selected as an illustration of the second geometrical property because the crystal structure concerned belongs to the same system of symmetry as the parent closest-packed assemblage from which it is derived, namely, the cubic system, and the process is therefore comparatively easy to trace. The application of the same property to other cases in which this latter relation does not exist is referable to a modifying cause which is described in connexion with the examples which follow.

Sodium Nitrate, NaNO₃.

The modification of sodium nitrate stable at the ordinary temperature belongs to the holohedrally rhombohedral system and exhibits

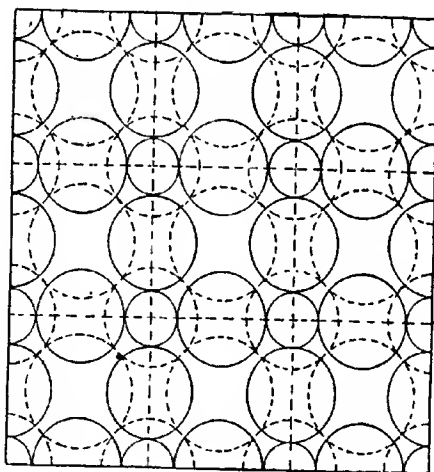
$\alpha = 102^\circ 47'$ or $a:c = 1:0.8276$ (Brooke, *Ann. Phil.*, 1823, 21, 452).

A close-packed assemblage of the valency composition of this salt is connected with a closest-packed assemblage of bivalent spheres of influence by the second geometrical property, in just the same way as is the assemblage representing barium nitrate. In both cases each of one-fourth of the total number of bivalent spheres is replaced by a sphere of trivalent size; the sodium nitrate assemblage is derived by adding, in accordance with the second geometrical property, one sphere of univalent size, representing sodium, for each trivalent nitrogen sphere so added, whilst the barium nitrate assemblage has been derived by similarly adding one bivalent sphere, representing barium, for each two nitrogen spheres. Double as many cavities have thus to be provided for the accommodation of the sodium spheres as had to be found for the barium spheres, but as the former are approximately of one-half the size of the latter, the total volume of the spheres representing the metallic element is the same in both cases.

When the cubic cells of the root assemblage are enlarged to the same extent as in the previous case, namely, in the volume proportion of 4:5, the required number of large cavities is provided by moving the oxygen spheres until their centres occupy the points of bisection of the enlarged cell edges; the process of expansion, which may be supposed to draw the oxygen spheres equally away from all the cell corners, will similarly enlarge all the cavities at the centres of the octahedral groups of six oxygen spheres surrounding those corners. The magnitudes of the spheres which just fit into the cavities occurring in a skeleton assemblage of oxygen spheres thus expanded are shown in Fig. 5. The larger spheres are, as in the previous case, larger than the trivalent spheres to be accommodated, although the disparity is now less; the small spheres centred at the cube corners are, on the other hand, much smaller than the univalent spheres which have ultimately to replace them. The assemblage of Fig. 5, like the parent assemblage, is of the holohedral cubic type of symmetry, and it has to be ascertained what modification of it results when nitrogen spheres, of trivalent magnitude, and sodium spheres, of univalent magnitude, are used in place of those depicted. Inspection of Fig. 5 shows that the length of the edge of a cube cell is the sum of the diameters of a small sphere, centred at the cube corner, and an oxygen sphere situated at the middle of a cube edge. On substituting the small and the large spheres by sodium and nitrogen spheres of the magnitudes indicated by the valencies, whilst retaining the kind of arrangement, the cell edges must necessarily be increased in length, since the univalent sodium spheres are larger than the small spheres of the assemblage of Fig. 5; the volume of the cell has, however, to

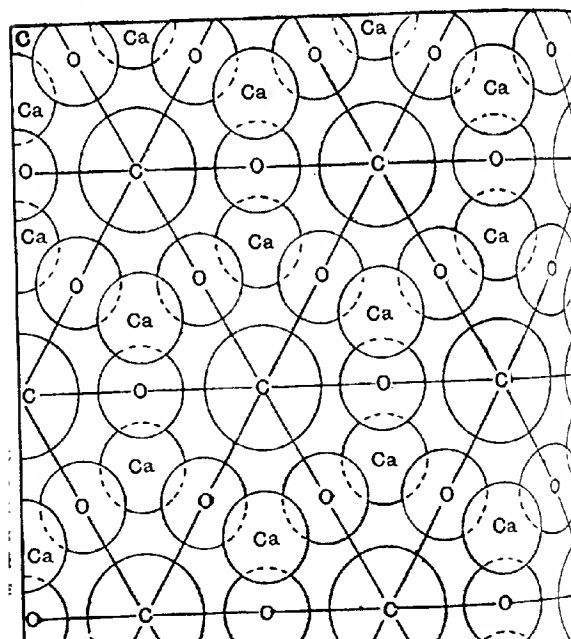
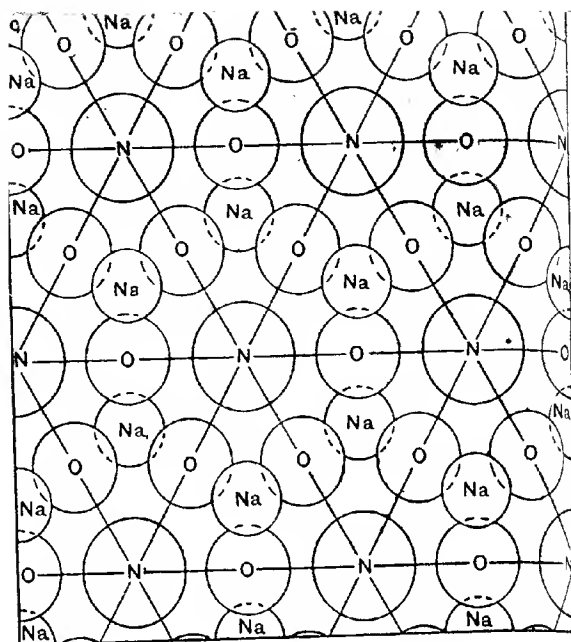
remain unaltered because it represents the molecular valency volume, 10, of sodium nitrate. The retention of the method of grouping, and the preservation of the same volume, will thus involve a distortion of the cube cells to rhombohedra, since this is the kind of distortion which, whilst keeping the edges of the cells equal, gives them greater length in proportion to the cell volume. It is therefore established that for the prescribed cell volume, if the grouping above described is adopted, rhombohedral space-lattices will take the place of the cubic ones found in the assemblage of Fig. 5. The amount of distortion, upon which the angle of the rhombohedron depends, will evidently be that which gives maximum closeness of packing under the given

FIG. 5.



conditions; it remains to ascertain, first, whether the arrangement thus reached is a stable one, and, if not, what modification should take place in order that it may become stable, and, secondly, the nature of the symmetry displayed when stable equilibrium is reached.

In the passage of the assemblage of Fig. 5 to rhombohedral symmetry, one of the four trigonal axes becomes the principal axis of the modified system, and it is convenient to depict the latter by its projection upon the plane perpendicular to this principal axis. An assemblage of rhombohedral form, in which the trivalent nitrogen spheres are centred at the cell centres, the bivalent oxygen spheres have their centres at the points of bisection of the cell edges, and the univalent sodium spheres are centred at the cell corners, is thus repre-



presented in Fig. 6.; the projections of three successive layers on the same area of a plane perpendicular to the trigonal axis are depicted, and are marked a, b, and c, respectively. The fourth layer has the same projection as the first, the fifth as the second, and so on. The spheres representing sodium, which lie immediately above and below each plane of centres of the nitrogen and oxygen spheres, are in each case indicated by continuous and non-continuous circles respectively; each sodium sphere is thus depicted twice over, so that those represented by continuous circles in Fig. 6a are also represented by discontinuous circles in Fig. 6b. The assemblage is of Barlow's type 52a₁. Trigonal axes pass through all centres of nitrogen and sodium spheres; digonal axes lie in the directions indicated by the straight lines in the figures, through all the nitrogen spheres, and also, parallel to these lines, through the centres of the sodium spheres. Centres of symmetry occur at all the sphere centres and midway between the centres of pairs of sodium spheres in planes parallel to those of the diagrams. The packing of the assemblage described is not so close as that of the closest-packed assemblage of equal spheres; the scale selected for the diagrams is obtained by making the content of the unit rhombohedral cell equal to the valency volume 10 of the salt, and the angles of this cell those of the cleavage rhombohedron of the crystalline mineral. Thus, if A is the longer face diagonal of this rhombohedral cell and C its axial body diagonal, since the content of the rhombohedron is $A^2C/2\sqrt{3} = 10$ and $A:C = a:c$, the values, $A = 3.472$ and $C = 2.873$, are obtained. These values are used as the scale to which the diagrams are constructed, and they involve a rather considerable flattening of the spheres at some of their contacts. If the volumes of the spheres representing sodium, oxygen, and nitrogen are respectively in the ratio of 1:2:3, and the rhombohedron angle adopted is that observed upon the crystals of sodium nitrate, the arrangement is seen to be practically stable as depicted by a stack of deformable spheres under pressure.

The marshalling shown above to be common to the cubic and the rhombohedral form of assemblage is the simplest possible of spheres of the three sizes indicated by the valencies, and present in the proportion represented by the composition, NaNO_3 , of the salt; the assemblage described is fairly close-packed. A slight adjustment is, however, possible, which increases the closeness of the packing without changing the marshalling; its occurrence involves the loss of some of the elements of symmetry, but retains the original crystal symmetry, namely, holohedrim of the rhombohedral system. The adjustment in question consists in moving each oxygen sphere along the line joining the two nitrogen spheres between which it lies until it touches one of them; all these movements are made symmetrically, and the result is depicted in Fig. 7. In this diagram six different projections of six

consecutive layers of nitrogen and oxygen spheres on the same area are shown by the sections a, b, c, d, e, and f, respectively; the sodium spheres which lie between the layers are, as before, indicated twice over, and the projections a, c, and e present the opposite orientations to those of b, d, and f. In order to obtain a relative molecular volume comparable with that of the closest-packed assemblage of equal spheres, less flattening of the spheres at their points of contact is now requisite; the conversion of the component spheres into polyhedra by a general compression consequently involves less departure from sphericity than before the adjustment.

It is suggested that the assemblage thus finally arrived at is in stable equilibrium when the rhombohedron angle closely approximates to that of sodium nitrate. The scale employed in the diagrams represents the rhombohedral unit cells as of the valency volume, $W = 10$, of sodium nitrate, and the unit of volume has therefore the same content as a dodecahedral cell of a closest-packed assemblage of spheres of univalent magnitude; the rhombohedron angle is represented as having the observed value of $\alpha = 102^\circ 47'$.

The elements of symmetry remaining after the final adjustment are (a) all the original trigonal or principal axes, (b) those of the digonal axes which intersect both nitrogen and oxygen spheres, and (c) the centres of symmetry situated at the centres of the sodium spheres, and those which lie in the planes of the latter but midway between them; the other elements of symmetry previously enumerated are destroyed by the adjustment. The type of symmetry presented is that numbered 52a₂ in Barlow's list (*Zeitsch. Kryst. Min.*, 1894, 23, 47).

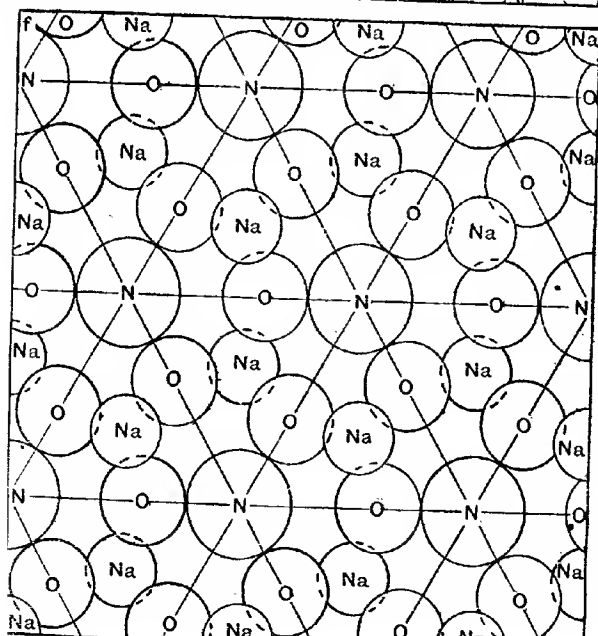
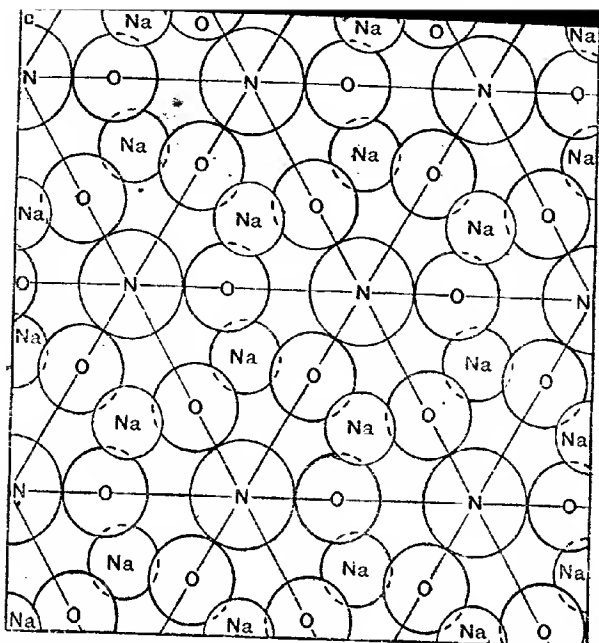
Reference has been already made to the fact that the rhombohedral sodium nitrate and the orthorhombic rubidium nitrate are, dimensionally, so closely related that the axial ratios of the former can be transposed into a form almost identical with those of the latter, namely:

Rubidium nitrate	$a:b:c = 1.7366:1.07106.$
Sodium nitrate	$a:b:c = 1.7320:1.07151.$

From this close correspondence it is concluded that the rhombohedral sodium nitrate is divisible into similar layers of a form which can be employed in building up the orthorhombic structure of rubidium nitrate.

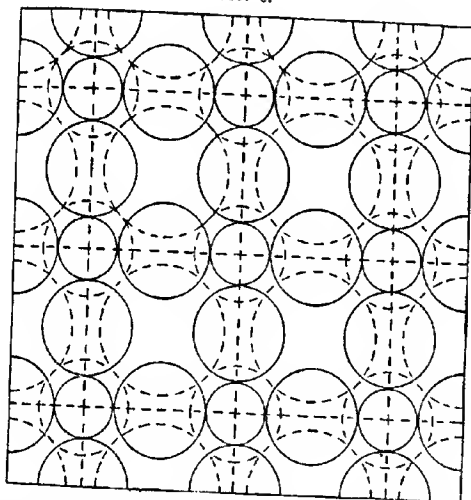
The Rhombohedral Form of Calcium Carbonate.

Calcite, the holohedral rhombohedral modification of calcium carbonate, CaCO_3 , is crystallographically so nearly identical with sodium nitrate that the resemblance is greater than that commonly displayed by the crystals of isomorphous substances. This resemblance, as already indicated (*Trans.*, 1906, 89, 1731), is associated with a relationship in composition between the two substances which affords



a simple illustration of the second geometrical property of close-packed assemblages. In the derivation of the cubic assemblage of Fig. 5, in connexion with sodium nitrate, from the cubic closest-packed assemblage of spheres each of volume two, the unit cubic cells of the latter were expanded in the volume ratio $8:10=4:5$, because the group of four bivalent spheres of total volume 8 in the latter assemblage were to be replaced by the group, NaNO_3 , of valency volume, $W=10$. On expanding the original cubic cells to an extent determined by the greater valency volume, $W=12$, of calcium carbonate, namely, in the ratio $8:12=2:3$, and, as before, introducing spheres of the largest

FIG. 8.



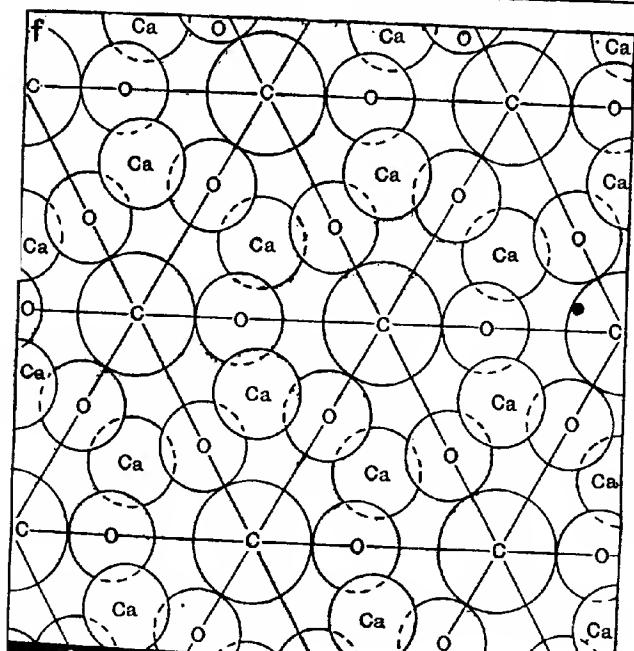
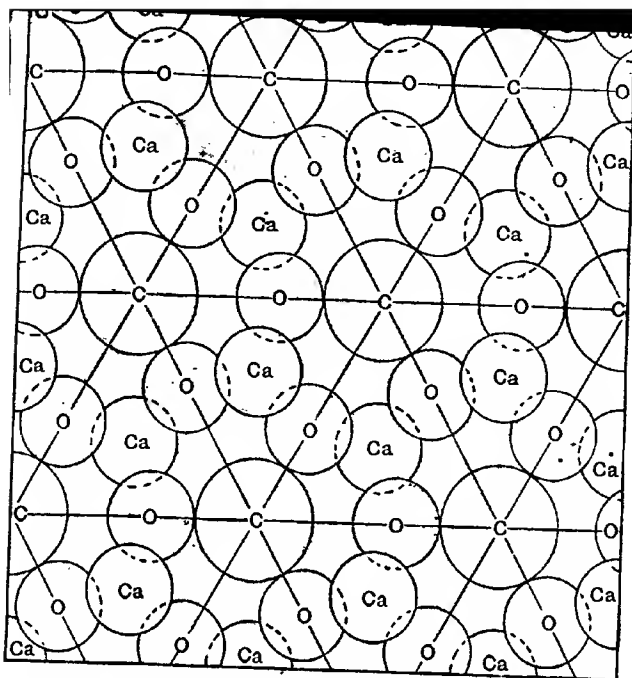
possible size into the two kinds of principal cavities thus made, the arrangement of Fig. 8 is obtained; in this the large spheres are rather larger than those representing quadrivalent carbon and the small spheres are smaller than those representing the bivalent calcium sphere. On replacing the large and small spheres by quadrivalent carbon and bivalent calcium spheres, keeping the cell volume constant, the assemblage passes to the rhombohedral one of Fig. 9, just as is described above in connexion with sodium nitrate. A final slight adjustment such as led to closer packing by movement of the oxygen spheres in the sodium nitrate assemblage also leads to closer packing in the case of the calcite assemblage; the rhombohedral assemblage representative of calcium carbonate is depicted in the six sections of Fig. 10.

The marshalling of the assemblages of rhombohedral symmetry which have been derived for sodium nitrate and calcite is still that of the original assemblage of bivalent spheres from which they were derived. In the latter assemblage each fourth sphere of volume t was replaced by a nitrogen sphere of volume three, an operation which when not accompanied by remarshalling, left cavities capable of accommodating an equal number of sodium spheres of volume on the sodium nitrate assemblage was thus derived. When each fourth bivalent sphere in the original assemblage was replaced by a carbon sphere of volume four, without remarshalling, cavities were produced which accommodated an equal number of calcium spheres of volume two. The relations here described afford a simple illustration of the second geometrical property of close-packed assemblages; the case differs somewhat from that exemplified by the cubic barium nitrate in that, in the present one, a marshalling of highest symmetry, the cubic, is compelled to assume the lower crystal symmetry of the rhombohedral system. The reason of this is that in certain linear directions the assemblage is unyielding and resists compression, namely, along the edges of the cubic space units as above explained; it is traceable to the fact that all the centres of the constituent spheres occupy singular points of a highly symmetrical character and are thus similarly related to many surrounding spheres. The only adjustment which, whilst it allows a slight contraction to occur in the linear directions referred to, does not diminish the closeness of packing to a greater extent in other directions, appears to be the one above described involving the movement of the oxygen spheres; it is noteworthy that this does not further lower the crystal symmetry.

Twinning of Sodium Nitrate and Calcite.

Crystals of sodium nitrate and calcite can be artificially sheared without destroying their identity in such a manner as to reproduce the original crystal form; this property will now be shown to characterize the assemblages attributed above to these substances.

The six sections of Figs. 7 and 10 represent projections of the assemblages on the basal plane (111); in any one of these sections, for instance, 7b, the six sodium spheres, three above and three below, surrounding immediately any nitrogen sphere, together with the sodium spheres shown above and below that nitrogen sphere in two adjacent sections, 7a and 7c, mark the eight apices of a cleavage rhombohedron of the crystal. The planes containing two opposite edges of a cleavage rhombohedron, which do not contain the principal axis, constitute the form $\{110\}$, and are the gliding planes on which sodium nitrate and calcite crystals can be sheared and artificially



twinned with such facility. The projection of a section of the sodium nitrate assemblage of Fig. 7 upon the plane (110) is shown in the lower part of Fig. 11; thus regarded, the assemblage is made up of similar layers each containing nitrogen, sodium, and oxygen spheres in equal numbers, with centres all lying in the same plane, and between which are intercalated layers consisting of the remaining two-thirds of the oxygen spheres. The continuous circles of this part of Fig. 11 represent a layer of the first kind, consisting of nitrogen, sodium, and oxygen spheres, and the next layer of identical composition is represented by the similar arrangement of non-continuous circles; the oxygen spheres intercalated between the pair of such layers are indicated by double non-continuous circles. An elevation of the system of which the stratum thus represented forms a part, and showing a double layer, the plane of which is perpendicular to that of the lower part, is depicted in the upper part of Fig. 11. Where the double circles are of two kinds, continuous and non-continuous, they do not represent a single sphere, but a larger and a smaller sphere one behind the other.

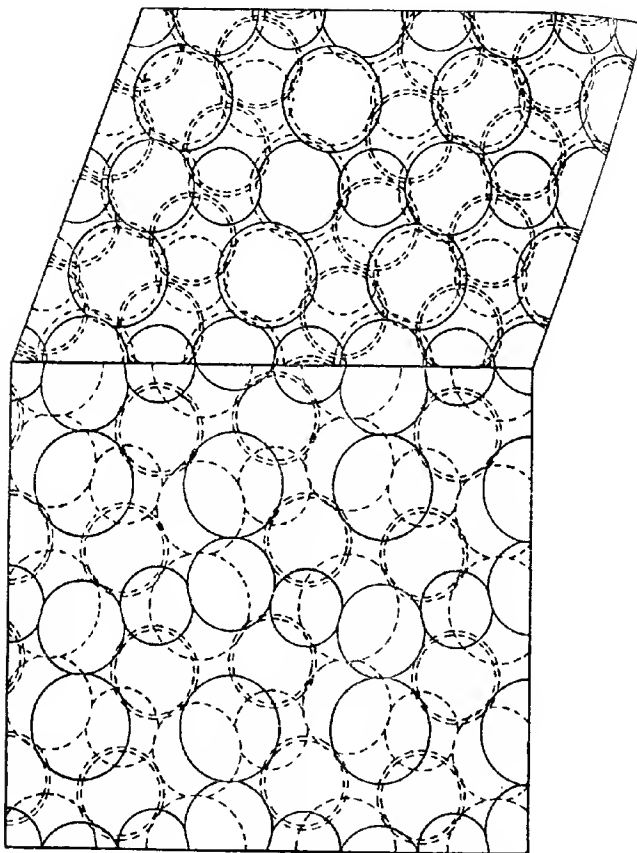
In the building up of the sodium nitrate assemblage in the manner indicated by the compositions and relative arrangement of the three layers depicted in Fig. 11, a choice of orientation is offered after each layer composed of nitrogen, sodium, and oxygen spheres has been deposited. Thus, starting with the layer represented by non-continuous circles in Figs. 11 and 12, the succeeding layers may be deposited as indicated by the double non-continuous and continuous circles either of Fig. 11 or of 12; the orientation of the one mode of growth is opposite to that of the other and is further illustrated by the projections shown in the upper parts of Figs. 11 and 12. The latter diagrams, in which most of the component spheres lie in contact in straight lines, indicate clearly how, by a simple rolling movement of the spheres upon each other, the orientation of Fig. 11 can be converted into that of Fig. 12.

The mechanism of the artificial twinning of sodium nitrate is thus clearly indicated, and the only further requisite is that the shear of the portion on one side of a gliding plane, (110), shall take place without dislocating the connexion with the unaltered portion on the other side of this plane. If the assemblage under treatment were the unmodified more symmetrical one of Fig. 6 the symmetry of arrangement would ensure this; as it is, some mutual adjustment of the intermediate oxygen spheres has to occur in the modified assemblage at the twin plane. The nature of this adjustment is indicated in the discussion of the crystal structure of potassium nitrate given below.

In connection with the derivation of the rhombohedral sodium

nitrate assemblage it has been shown that the marshalling of the final arrangement is still that appropriate to an assemblage of spheres in cubic symmetry. The passage from cubic to rhombohedral symmetry necessitates the distinction of one of the four trigonal cubic axes as

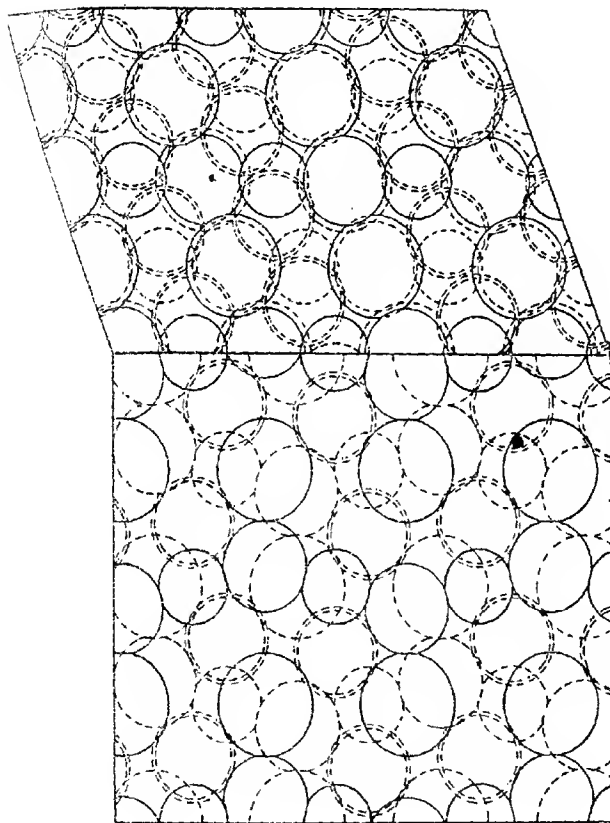
FIG. 11.



the principal or trigonal axis in the rhombohedral assemblage; after one of the four trigonal cubic axes has been thus distinguished from the other three as a direction of symmetry it is still possible, by the operation of some influence such as is involved in a shear of the above-described kind, to convert either of the three previously dis-

carded trigonal cubic axes into the principal axis of the rhombohedral assemblage. The change thus effected does not when completed alter the configuration of the assemblage, but brings about a change of orientation which corresponds exactly with that produced by the

FIG. 12.



artificial twinning of sodium nitrate. It is obvious, without the exhibition of farther diagrams, that the mechanism which illustrates the artificial twinning of sodium nitrate elucidates in precisely the same way the artificial twinning of calcite.

Potassium Nitrate, KNO₃.

Potassium nitrate crystallises in the orthorhombic system with $a:b:c=0.5910:1:0.7010$, and crystallographically closely resembles aragonite, the orthorhombic modification of calcium carbonate, just in the same way as the rhombohedral substances sodium nitrate and calcite resemble each other; the two orthorhombic crystal forms, like the two rhombohedral ones, are connected through the second geometrical property (Trans., 1906, 89, 1732).

The marshalling of the orthorhombic assemblage suggested for potassium nitrate is derived by an intimate molecular twinning of the rhombohedral assemblage above assigned to sodium nitrate, the change of orientation from stratum to stratum occurring at every corresponding layer of the three kinds of spheres which lies parallel to one plane of the form $\{110\}$. It has been shown in connexion with artificial twinning that the stratum of the sodium nitrate assemblage, which is parallel to the plane (110), and is depicted in the lower part of Fig. 11, is capable of alteration by shear; the shear produces identically the same arrangement of the constituent spheres, but changes the orientation, and it was suggested that a portion of the rhombohedral assemblage can be sheared without dislocating its connexion with the unsheared portion, if a slight adjustment of the spheres occurs at the gliding plane which becomes the twin plane. When every one of the layers composed of three kinds of spheres, as shown in the lower part of Fig. 11, becomes a twin plane, the marshalling of the assemblage represented in Figs. 11 and 12 becomes transformed into that represented in Fig. 13. The close resemblance of the constituent layers of Fig. 13a to those of the rhombohedral assemblage as shown in Fig. 11 is very apparent, and the requisite adjustment of the two-thirds of the oxygen spheres, which makes the twin planes planes of symmetry, is seen to be slight. Fig. 13b depicts the projection on a plane perpendicular to that of Fig. 13a, and a comparison with Figs. 11 and 12 suffices to indicate how the intimate twinning occurs.

The assemblage of Fig. 13 is of orthorhombic symmetry, and satisfies the conditions embodied in the axial ratios and other geometrical data of the orthorhombic potassium nitrate; it is indeed drawn to the scale of the equivalence parameters of the substance, calculating the latter values from the axial ratios in the form $a:b/2:c$, and taking the valency volume $V=10$. The equivalence parameters of potassium nitrate are thus calculated as $x:y:z=2.152:1.821:2.553$, and these values are marked on Fig. 13. The process of twinning by which the assemblage has been derived is, of course, to be regarded as a mere

geometrical device; its only physical meaning is that it shows that the isopolymorphously related substances, the rhombohedral sodium and the orthorhombic potassium nitrate, can be built up as the results

FIG. 13b.

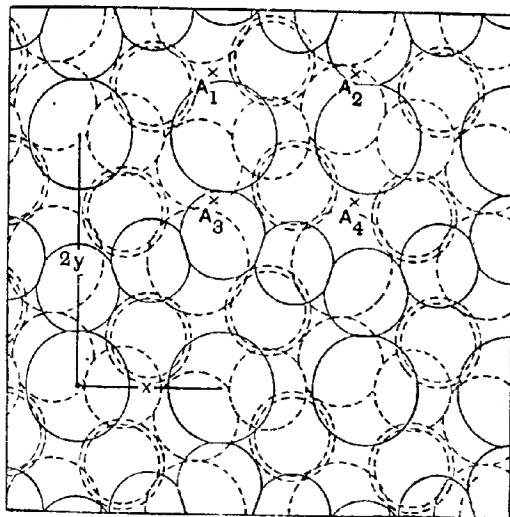
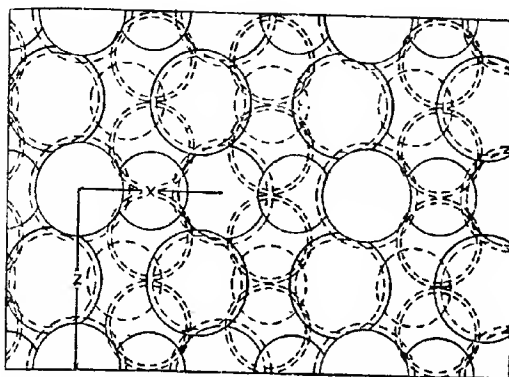


FIG. 13a.

of alternative modes of superposing layers of similar configuration. The potassium nitrate assemblage described possesses the symmetry of Baulow's type $\{54a_2\}$; it contains digonal screw axes in the three

directions mutually at right angles, namely, (1) perpendicular to the plane of Fig. 13a, through points such as A_1, A_2, A_3, A_4 , (2) parallel to the plane of Fig. 13a through the centres of the smallest, and also through those of the largest, spheres, and (3) parallel to the direction of y , midway between the planes of set (1) and also midway between those of set (2). Centres of symmetry lie on the axes (1) in planes containing the axes (3).

A rhombohedral modification of potassium nitrate can exist (Frankenheim, *Pogg. Ann.*, 1837, 40, 447), but is so unstable at the ordinary temperature that no goniometric measurements have been made; the crystallographic dimensions of the orthorhombic and rhombohedral modifications of the salt cannot therefore be directly compared. Such a comparison can, however, be instituted between the dimensions of the rhombohedral sodium nitrate and the isopolymorphously related and orthorhombic potassium nitrate. According to the relation suggested above as holding between the assemblages of these two substances, the length of the rhombohedron edge, the longer semi-diagonal of a rhombohedral face, and the distance between two opposite rhombohedron edges which intersect the obtuse angles constitute three rectangular dimensions which should be approximately reproduced as the equivalence parameters, $x:y:z$, of the corresponding orthorhombic assemblage; the ratio of these is identical with the axial ratios $a:b/2:c$ of the orthorhombic substance. A closer comparison of the same kind can be made between the axial ratios of the two polymorphously related forms of calcium carbonate, because the assemblages representing these substances must be related in just the same way as the rhombohedral sodium nitrate and the orthorhombic potassium nitrate assemblages figured above. The rhombohedral calcite, with $\alpha = 101^\circ 55'$, and the orthorhombic aragonite, with $a:b:c = 0.6224:1:0.7206$, are depicted by sets of diagrams corresponding exactly feature by feature with those given above for sodium and potassium nitrates. In the unit rhombohedron cell of calcite, the length of the rhombohedron edge, the longer semi-diagonal of a rhombohedral face, and the distance between two opposite rhombohedron edges which intersect the obtuse angles should therefore be approximately in the ratio of the axial ratios $a:b/2:c$, determined on aragonite.

The rhombohedron angle of calcite is $74^\circ 55'$, and from this the plane angle, $A_1A_2A_3$, of the face of a calcite rhombohedron, $AAAAA_1A_2A_3$ (Fig. 14), is calculated as $78^\circ 5'$. The longer diagonal of the rhombohedron face is A_2A_4 , and, in the plane $A_2BA_4B_1$, which contains this diagonal and is perpendicular to the rhombohedron edge AA_1 , the length BB_1 is the distance between two opposite rhombohedron edges which intersect the obtuse solid angles of the rhombo-

hedron; the plane angle BA_2B_1 is the rhombohedron angle $74^\circ 55'$. Taking $OA_2 = 1$, $OB = \tan \{(74^\circ 55')/2\} = 0.7662$, and $A_1A_2 = AA_1 = 1$, $\cos \{(78^\circ 5')/2\} = 1.2875$; one-half the latter value is 0.6437. The axial ratios,

$$a : b : c = 0.6437 : 1 : 0.7662,$$

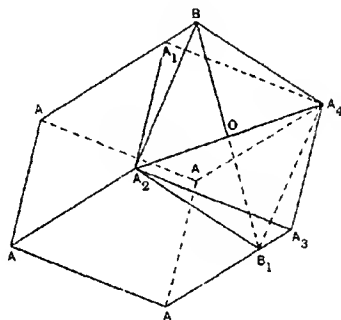
are thus obtained by calculation from the axial angle of calcite for comparison with the axial ratios of aragonite, namely,

$$a : b : c = 0.6224 : 1 : 0.7206.$$

It is obvious that the two sets of axial ratios are of the same order of magnitude.

The rhombohedral sodium nitrate is characterised by a rhombohedron angle of $73^\circ 30'$, from which the plane angle is calculated as $77^\circ 14'$. A

FIG. 14.



calculation similar to that made in the case of calcite leads to the axial ratios,

$$a : b : c = 0.6399 : 1 : 0.7467,$$

for comparison with the axial ratios of the orthorhombic potassium nitrate, namely,

$$a : b : c = 0.5910 : 1 : 0.7010.$$

As is to be expected from the difference in the metal present in the rhombohedral and orthorhombic salts, the last two sets of ratios are not in such fair agreement as those calculated from the rhombohedral and orthorhombic modifications of calcium carbonate. The reason why a greater discrepancy is observed among the equivalence parameters of the rhombohedral and orthorhombic carbonates than obtains in many other cases quoted may well be that when fitted together in different ways, the component layers in the structures have to experience a slight internal adjustment; the nature of this adjustment is shown, in the case of the nitrates and carbonates now under consideration, by comparing Figs. 11 and 13. A closer agreement is

presented in the case of the polymorphously related forms of silver iodide; the component layers are of a less complicated character in this case, and can be fitted together in the two different ways without any apparent internal adjustment.

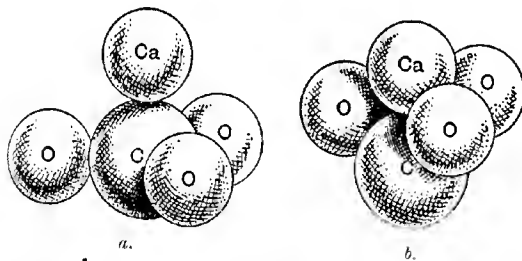
The scheme now put forward embraces, in addition to the rhombohedral and orthorhombic nitrates mentioned above, the rhombohedral minerals of the compositions MgCO_3 , FeCO_3 , ZnCO_3 , and MnCO_3 , and the hemihedrally rhombohedral dolomite, $\text{CaMg}(\text{CO}_3)_2$, and also the orthorhombic minerals of the compositions BaCO_3 , SrCO_3 , and PbCO_3 , together with the isomorphous mixtures $(\text{BaCa})\text{CO}_3$, classed under the name bromlite. The monosymmetric barytocalcite, $\text{BaCa}(\text{CO}_3)_2$, with $a:b:c=0.6255:1:0.7717$, $\beta=106^\circ 8'$, is morphotropically closely related to calcite (Arzruni, *Physik. Chem. d. Krystalle*, 1893, 295), and its structure may hence probably be derived by distortion from that of the latter. The relation between the dimensions of the rhombohedral sodium nitrate and the orthorhombic rubidium nitrate has been already pointed out (p. 1531). In connexion with the structure of dolomite, it should be noted that the unmodified assemblage depicted in Fig. 9 was suggested some years ago by one of the authors as the probable scheme of arrangement of the component atoms in calcite; the observation that dolomite, $\text{CaMg}(\text{CO}_3)_2$, displays a lower form of symmetry, namely, rhombohedral tetartohedral, with centro-symmetry, led to a reconsideration of the question and to the adoption of the slightly modified form shown in Fig. 10. When, in the latter, half the layers of calcium spheres are replaced by layers of magnesium spheres similarly situated so that layers wholly composed of one of these two kinds alternate with layers composed of the other kind, the diagonal axes of Fig. 10 are destroyed, and the lower form of symmetry presented by dolomite is obtained. The dolomite assemblage thus produced has the symmetry of Barlow's type 51a.

The slight differences in axial ratios or axial angles observed between members of the various isomorphous series of salts discussed above are, as in previous cases, to be attributed to the volumes appropriated by the spheres of atomic influence not being precisely proportional to the whole numbers representing the fundamental valencies of the elements concerned; the volumes of the spheres of atomic influence of the several bivalent elements thus differ slightly among themselves. It has been shown (Trans., 1907, 91, 1193) that in the case of the halogens such divergencies can be traced consistently throughout a whole series of compounds with the result that a definite conclusion is reached that the volume for iodine is the greatest, and those for bromine, chlorine, and fluorine are respectively smaller and smaller. Whether a particular salt belonging to the series dealt with above

will assume the orthorhombic or the rhombohedral form will, it is suggested, depend on which form of symmetry, with the precise volumes assumed by the spheres of atomic influence under the prevailing conditions, will lead to the least departure from sphericity of the latter.

Both the calcite and aragonite assemblages described above may be homogeneously partitioned into highly symmetrical units having the composition CaCO_3 and the configurations depicted in Fig. 15, *a* and *b*; both assemblages may be regarded as built up by homogeneously fitting together either kind of these units in accordance with the appropriate crystal symmetry, slight distortion being practised where necessary, as in cases previously described. The rhombohedral sodium nitrate and the orthorhombic potassium nitrate assemblages described and figured above each similarly yield two kinds of highly symmetrical unit; these possess the composition NaNO_3 or KNO_3 , and possess

FIG. 15.



configurations identical with those depicted in the case of calcium carbonate.

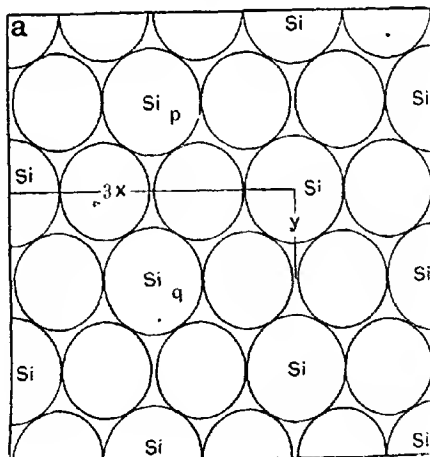
The intimate structural relationship existing between the rhombohedral forms of sodium nitrate and calcium carbonate has been traced in the foregoing pages to the operation of the second geometrical property of close-packed assemblages. A case of exactly the same kind is furnished by the morphotropic relationship between the orthorhombic sulphates of the bivalent metals and perchlorates, &c., of the alkali metals, *e.g.*, between barium sulphate, BaSO_4 , and potassium perchlorate, KClO_4 . When, in the assemblage appropriate to barium sulphate, the bivalent barium sphere of influence is replaced by the smaller univalent sphere of influence of potassium, the simultaneous substitution of the bivalent sulphur sphere by the univalent chlorine sphere can occur, in accordance with the second geometrical property, in such a manner that the original marshalling is retained; the axial ratios are in this case but slightly altered and the crystal symmetry remains

unchanged (compare Barker, *Min. Mag.*, 1906, 14, 235; 1908, 15, 50). It is important to note that potassium permanganate, KMnO_4 , is isomorphous with potassium perchlorate, KClO_4 , so that the manganese sphere of influence appropriates a volume comparable, for purposes of close-packing, with that of the univalent chlorine. The isomorphism existing between the rhombohedral calcite, CaCO_3 , and rhodocrosite, MnCO_3 , shows, however, that the bivalent sphere of influence of calcium is crystallographically replaceable by the manganese sphere. These apparently contradictory indications, namely, that manganese can replace either a bivalent or a univalent atom, point to the conclusion that the manganese sphere appropriates in an assemblage a volume intermediate between those occupied by a univalent and a bivalent atom; the correctness of this conclusion is strongly confirmed by a consideration of the complex valency relations of manganese.

The Polymorphous Forms of Silica.

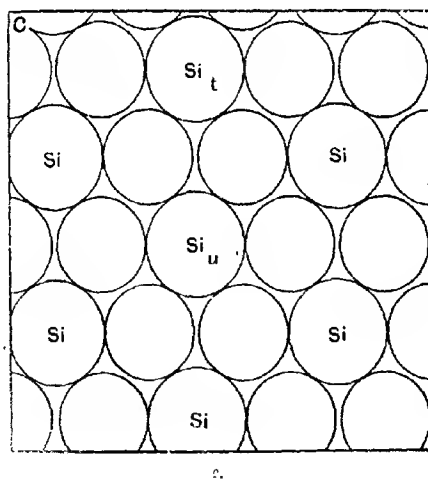
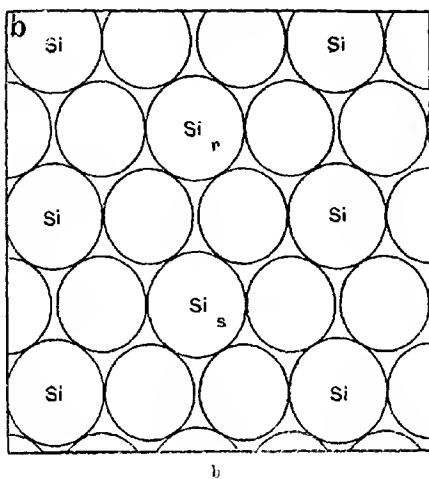
A very simple structure may be attributed to the constituent layers from which the crystalline polymorphous forms of silica, quartz, and tridymite are built up; this simplicity of layer structure, as in the case of silver iodide, is consistent with the close numerical correspondence between the axial ratios of the two minerals which has been already remarked (p. 1530). The assemblages appropriate to the two substances consist of spheres of the bivalent magnitude repre-

FIG. 10.



a.

FIG. 16 (*continued*).



senting silicon and oxygen ; the silicon spheres are regarded as slightly larger than those of oxygen, but the mean valency volume of a sphere of the assemblage is taken as 2. The equivalence parameters for the trigonal trapezohedral quartz and the orthorhombic tridymite are

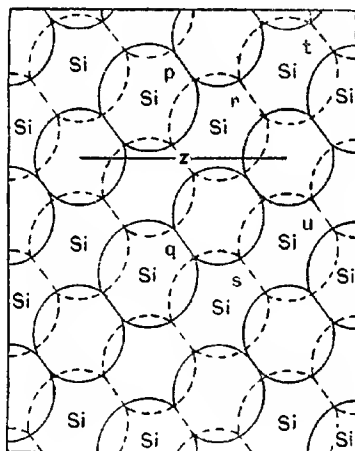
conveniently calculated from the axial ratios in the form previously given, namely,

	$a : b : c.$	$x : y : z.$
Quartz	0.5774 : 1 : 1.2701	1.466 : 1.269 : 3.221
Tridymite	0.5774 : 1 : 1.2716	1.465 : 1.269 : 3.227

first, however, dividing the length b by two; the valency volume, for the molecule SiO_2 , is taken as $W = 6$.

In the case of quartz the spheres of the appropriate assemblage present the marshalling of the cubic closest-packed assemblage of equal spheres (Trans., 1907, **91**, 1152), one-third of those of a triangularly arranged layer consisting of silicon spheres and two-thirds

FIG. 17.

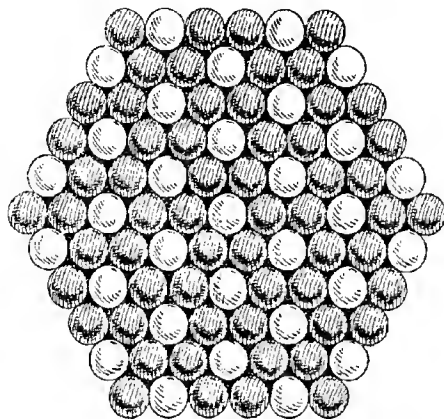


of oxygen spheres. The nature of the assemblage is shown by the three consecutive layers of Fig. 16, a, b, and c, and the corresponding elevation of Fig. 17; the symmetry of the assemblage thus constituted is that of the trigonal trapezohedral crystal class to which quartz belongs.

The triangular arrangement of spheres in a layer of Fig. 16 is that depicted in Fig. 18, in which the lightly shaded spheres represent those of silicon. On mutually arranging layers of this kind in accordance with the marshalling of the cubic closest-packed assemblage, that is to say, giving the layers the relative arrangement indicated by Fig. 16, a, b, and c, the resulting assemblage presents the appearance shown in rough perspective in Fig. 19. It will be seen that the spheres of one kind form staircase spirals in this assemblage,

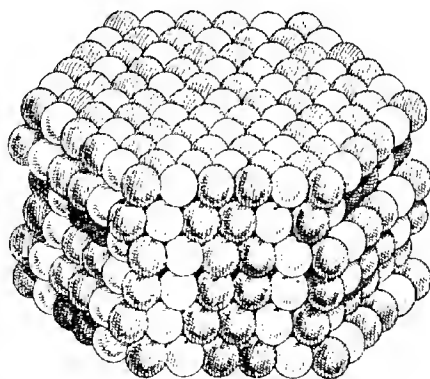
and that, depending upon the configuration of the mutual arrangement of the first three layers, an assemblage representing either right- or left-handed quartz may be built up. The two kinds of interpenetrant

FIG. 18.



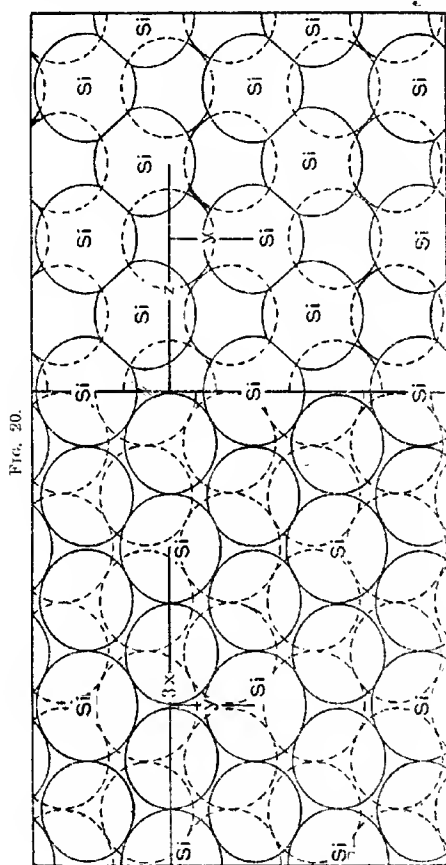
twinning commonly observed with quartz follow immediately from the mode of regarding the structure now put forward.

FIG. 19.



The assemblage representing the orthorhombic tridymite is derived by arranging layers identical with those of Figs. 16 and 18 in the marshalling of the hexagonal closest-packed assemblage of equal

spheres; it is illustrated in plan and elevation by Fig. 20 and in the rough perspective sketch of Fig. 21. This assemblage possesses holohedral orthorhombic crystal symmetry, and, as is seen from Fig. 21, the spheres of one kind form zigzags, devoid of enantiomorphism, within the structure. The equivalence parameters stated

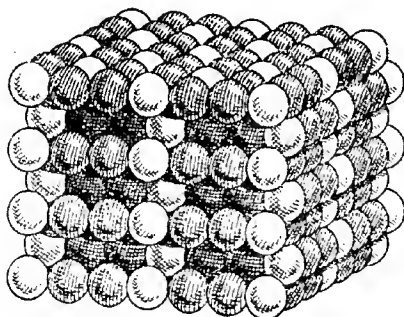


above are indicated as the translations in the diagrams representing the two minerals.

In the diagrams relating to the last two assemblages, as in those given for calcium carbonate and related substances, certain spheres are more or less flattened at the points of contact with others, but the

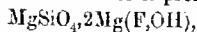
flattening is small in amount. The cause of the occurrence of this kind of modification will be interpreted in various ways in different cases. Thus, if two kinds of spheres can be distinguished in an assemblage such that the one kind makes but few contacts with neighbouring spheres whilst the other kind makes a large number of such contacts, flattening of the former should occur in order that the mutual arrangement of the centres of the spheres shall be preserved in the assemblage derived by the application of a general pressure which eliminates the interstitial space. Whilst the representation of flattening such as this is thus rendered necessary in certain cases, in others the flattening is associated with a discrepancy between the dimensions of the assemblage as measured and as deduced. In the case of the polymorphously related forms of silica the latter applies, but our ignorance of the exact volume relationship holding between the

FIG. 21.



spheres of atomic influence of silicon and oxygen hinders any precise investigation of the matter.

In a previous paper (Trans., 1906, 89, 1686) we have shown that the discussion of the equivalence parameters elucidates immediately the remarkable morphotropic relationship observed between chondrodite, $\text{Mg}_3(\text{SiO}_4)_2 \cdot 2\text{Mg}(\text{F},\text{OH})$, humite, $\text{Mg}_3(\text{SiO}_4)_3 \cdot 2\text{Mg}(\text{F},\text{OH})$, and diiclunite, $\text{Mg}_7(\text{SiO}_4)_4 \cdot 2\text{Mg}(\text{F},\text{OH})$. These minerals form a homologous series of which the first member is proectite,



and the homologous increment has the composition of forsterite, Mg_2SiO_4 . In calculating the equivalence parameters of these substances we originally assigned to silicon the valency volume $W=4$, which is in discordance with the volume, $W=2$, given to it in the present paper. It happens, however, that in the humite series, both the first member and the homologous increment contain silicon in such

proportions as to render the morphotropic relation very insensitive to a change in the valency volume assigned to this element. It consequently results that the calculation of the equivalence parameters based on the value $W=4$ or 2 for silicon gives an almost constant value for the ratio z/W . The alternative values thus obtained are given below.

For $Si=4$:

	W.	x	:	y	:	z	z/W .
Chondrodite	38	2.4249	:	2.2323	:	7.0199	0.18473
Humite	54	2.4278	:	2.2475	:	9.8965	0.18327
Clinohumite.....	70	2.4349	:	2.2540	:	12.7547	0.18221

For $Si=2$:

	W.	x	:	y	:	z	z/W .
Chondrodite	34	2.3367	:	2.1510	:	6.7644	0.19895
Humite	48	2.3318	:	2.1610	:	9.5155	0.19821
Clinohumite.....	62	2.3334	:	2.1646	:	12.2491	0.19759

The values of z/W obtained with the volume $Si=2$ agree distinctly better among themselves than do the values got with $Si=4$. These and other indications which suggest that the fundamental valency of silicon is 2 are significant because, if they are to be trusted, it would appear that carbon is the only element which has a fundamental valency so large as 4. The exceptional nature of carbon and the fact that this element is not known to be isomorphously replaceable by any other lend support to this suggestion.

As before, the author's thanks are due to the Committee of the Municipal School of Technology for permitting the blocks illustrating the paper to be made in the school, and to Messrs. Chas. W. Gamble and R. B. Fishenden, of the Photographic and Printing Crafts Department, for the care with which they have carried out the work.

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VICTORIA UNIVERSITY OF MANCHESTER.

CL.—The Action of Nitrous Gases on Dicyclopentadiene.

By ALEXANDER RULE.

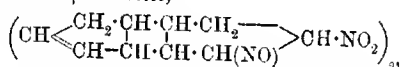
In a previous paper (Trans., 1906, 89, 1339) the author described several new compounds of dicyclopentadiene, but deferred mention of derivatives obtained by the action of nitrous gases on the hydrocarbon by arrangement with Dr. Wieland, of Munich. The work described in the present paper was carried out in Jena and published as a

university dissertation, and as Dr. Wieland has now published a full account of his own work, the author desires to give briefly the results previously obtained by him, in working on the hydrocarbon.

The gases evolved by the action of concentrated nitric acid on arsenic trioxide act vigorously on dicyclopentadiene in ethereal solution, and if the latter is kept cool in a freezing mixture two crystalline substances separate, together with amorphous products, the nature of which was not ascertained. The crystalline products were identified as the ψ -nitrosite and the dinitro-derivative of the hydrocarbon: the yield obtained never amounted to more than 20 to 25 per cent. of the weight of hydrocarbon used.

The mixture was separated by extraction with boiling alcohol, in which the dinitro-derivative readily dissolves, whilst the ψ -nitro site is only sparingly soluble. The residue was washed with hot alcohol and recrystallised from chloroform; the product consisted of small colourless needles melting at 147° (Wieland gives $144-146^{\circ}$).

Dicyclopentadiene ψ -nitrosite,



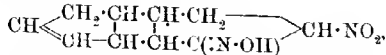
is insoluble in ethyl alcohol, ether or acetic acid, but dissolves in hot toluene, giving a bright green solution, which on cooling becomes almost colourless without crystallisation taking place. This is also the case with other solvents such as aniline, and therefore the substance belongs to the class of bimolecular nitroso-compounds which are dissociated with relative ease (*Ber.*, 1903, 36, 3090).

When treated with bromine in chloroform solution the substance forms a dibromide which is sparingly soluble and melts and decomposes at 152°.

Dilute acids are without action on the substance even on boiling; cold concentrated sulphuric acid dissolves it unchanged, but on warming, a violent evolution of sulphur dioxide takes place with complete charring.

The constitution of the nitrosite follows with certainty from its behaviour towards alkalis and amines, and from its conversion, on boiling with alcohol, into a nitro-oxime.

Nitroisonitrosodihydrodicyclopentadiene,



results when the ψ -nitrosite is boiled for some hours with alcohol, but the reaction takes place even more rapidly when an alcoholic solution of aniline is used. The reaction is over when the ψ -nitrosite is completely dissolved. The alcohol is then removed by distillation and

the residuc acidified slightly with dilute sulphuric acid. A viscid oil remains undissolved, which after a short time solidifies completely and may be recrystallised from benzene.* The product consists of fine short needles, melting at about 121° and soluble in most solvents, but only sparingly so in water:

0.1324 gave 15.6 c.c. N_2 (moist) at 20.5° and 745 m.m. $N = 13.33$.

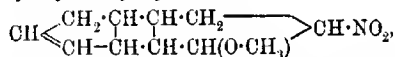
$C_{10}H_{12}O_3N_2$ requires $N = 13.46$ per cent.

Prolonged boiling with dilute sulphuric acid converts the nitro-oxime into hydroxylamine and a nitro-ketone, the former being recognised by reduction of Fehling's solution. The yield of the latter is very poor on account of the simultaneous formation of resinous products. It crystallises from the sulphuric acid solution on concentration, in small brownish prisms and plates, which after recrystallisation from water melt at about 205° with decomposition.

The product is soluble in ether, alcohol or alkalis, giving yellow solutions with the latter; on warming the alkaline solution with zinc dust a base is obtained which is soluble in ether and reduces Fehling's solution.

The amount of the substance obtained was not sufficient for analysis, but from its behaviour it would appear to be undoubtedly a nitro-ketone.

Nitromethoxydihydrocyclopentadiene,



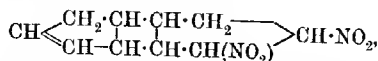
is prepared by boiling the ψ -nitrosite with excess of sodium methoxide. On concentrating sufficiently a colourless sodium salt separates out which is redissolved on the addition of a little water.

The nitro-derivative is isolated by precipitating from the alkaline solution with dilute sulphuric acid and dissolving the slightly greenish oil in ether. On evaporating the ether the oil rapidly solidifies to a crystalline mass, and by recrystallisation from light petroleum is obtained in thin plates which melt at 64° (Wieland gives 68°). This derivative is readily soluble in most organic solvents and is precipitated from its alkaline solution by mineral acids, but not by carbonic acid. By treating the alkaline solution of the nitro-compound with sodium nitrite (1 mol.) and acidifying in the cold with sulphuric acid, a brilliant blue ψ -nitrol is obtained as an oil which is readily soluble in ether and remains unchanged in ethereal solution for a considerable period, but on isolation rapidly decomposes. If the ethereal solution is dried with sodium sulphate and the ether allowed to evaporate, an

* Wieland's method of preparation resulted in the formation of a mixture of nitro-oxime and a substance of unknown constitution. The product melted at 118–123°. On purification the nitro-oxime melted at 136–138°.

intensely blue residue remains, which is no longer soluble in ether. When kept in a desiccator over sulphuric acid, it gradually swells up and evolves nitrous gases, leaving an amorphous residue. The latter, when freed as much as possible from resin by treatment with ether, gave on analysis $N = 9.09$ per cent.

Nitrodihydrodicyclopentadienyl nitrite,



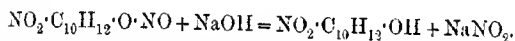
is formed simultaneously with the ψ -nitrosite by the action of nitrous gases on dicyclopentadiene and may be separated by extraction with hot alcohol. After recrystallisation from alcohol it is obtained in characteristic long toothed crystals, which have a slightly yellow tint and melt at 121° (Wieland gives 122°):

0.2069 in 42.75 ethylene dibromide gave $\Delta t -0.259^\circ$. M.W. = 220.

$\text{C}_{10}\text{H}_{12}\text{O}_4\text{N}_2$ requires M.W. = 224.

The compound is therefore unimolecular.

It is insoluble in cold dilute sodium hydroxide, but on warming, solution takes place rapidly, nitrous acid being at the same time eliminated; the compound is thereby characterised as an ester of nitrous acid:



On cooling, the clear solution solidifies to a crystalline mass which consists of the sodium salt of *nitrohydroxydihydrodicyclopentadiene*; this was collected, dried on porous plate, and recrystallised from diluted alcohol. After standing in a desiccator over sulphuric acid it still contained water which was removed on heating at $110-120^\circ$ until constant. The salt dissolves fairly readily in water, forming a neutral solution:

0.1535 dried at $110-120^\circ$ gave 0.0500 Na_2SO_4 . $\text{Na} = 10.54$.

$\text{C}_{10}\text{H}_{12}\text{O}_3\text{NNa}$ requires $N = 10.59$ per cent.

Nitrohydroxydihydrodicyclopentadiene is obtained on acidifying the solution of the sodium salt as a colourless semi-solid mass which shows very little tendency to crystallise.

The ψ -nitrol was also obtained. It dissolves in ether, giving a deep blue solution, and, like its methyl derivative already described, is very unstable. After drying the ethereal solution with anhydrous sodium sulphate and evaporating, the ether residue rapidly decomposes at the temperature of the water-bath, evolving nitrous gases and leaving brown amorphous products.

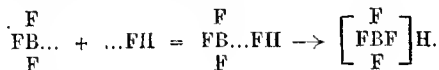
The work described in this paper was carried out in conjunction with Prof. P. Duden, to whom I wish to express my thanks for advice and suggestions.

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CLI.—*The Constitution of Co-ordinated Compounds.*

By SAMUEL HENRY CLIFFORD BRIGGS.

THE combination of hydrogen fluoride and boron fluoride is expressed by Werner in the following manner:

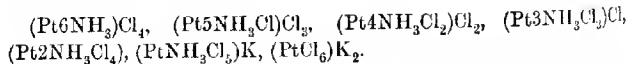


In the final state, as represented by the co-ordination formula $[\text{BF}_4]\text{H}$, the hydrogen atom is supposed to be united to the group (BF_4) as a whole rather than with any particular fluorine atom contained in it, and each of the four fluorine atoms is assumed to be combined in the same way as the other three.

Although such co-ordination formulæ have proved extremely useful for purposes of classification, they have been subjected to severe criticism (compare, for example, Hinrichsen, *Ahrens' Sammlung*, Vol. VII, p. 48). One serious objection to these formulæ appears to lie in the fact that they tell us so little of the way in which the affinities of the separate atoms are combined, and are consequently far inferior in utility to the valency formulæ which have been such an important feature in the development of organic chemistry.

In this paper an attempt is made to devise formulæ for co-ordinated compounds which will fulfil the conditions required by the experimental results of Werner and his colleagues, and, at the same time, indicate the manner in which the affinities of the atoms are disposed in the molecule.

For this purpose, the following series of compounds may be considered:



The electrical conductivity determinations of Werner and Miolati (*Zeitsch. physikal. Chem.*, 1893, 12, 35; 1894, 14, 506) have shown that the six atoms or groups within the brackets remain in combina-

tion with the platinum as a complex ion in aqueous solution, and are therefore directly united to the platinum in the undissociated compound.

Numerous investigations have proved that if the platinum is situated at the centre of an octahedron, the six atoms or groups in combination with it in the complex ion may be supposed to occupy the corners of the octahedron, whereas the dissociating atoms outside the brackets take up a position at a greater distance from the platinum, that is, outside the octahedron (Werner, *Zeitsch. anorg. Chem.*, 1893, 3, 267, &c.). The ionisable atoms are not supposed to be combined with any particular group X in the complex (PtX_6), but rather with the complex as a whole (*Zeitsch. anorg. Chem.*, 1893, 3, 325).

After the above description of Werner's theory as applied to the series of compounds in question, we may now consider the manner in which the atoms are held together in the molecule. In this series of seven compounds we have a complex which is first positive and quadrivalent, becoming successively trivalent, bivalent, univalent, and neutral. It then changes sign, becoming negative and univalent, and, finally, bivalent. Since the only unvarying constituent of the complex is the platinum, it would appear as if the platinum atom possessed two kinds of affinity, positive and negative, and was therefore able to form the basis for a cationic, as well as an anionic, complex.

The theory of duplex affinity, which was the foundation of the electrochemical system of Berzelius, has recently been revived by several chemists, particularly by Abegg (*Zeitsch. anorg. Chem.*, 1904, 39, 330; compare also Friend, this vol., 260; 1006). According to Abegg's theory every element has eight valencies, which are divided into two classes, namely, normal valencies and contravalencies. Platinum in the platonic compounds, for example, would have four positive normal valencies and four negative contravalencies.

Take now the compound $(\text{Pt}6\text{NH}_3)\text{Cl}_4$: with Werner's structural arrangement for this substance—that is, the platinum situated at the centre of an octahedron, with the six ammonia molecules at the corners and the chlorine atoms outside—the constitution may be written in three ways, namely, (1) the co-ordination formula $[\text{Pt}6\text{NH}_3]\text{Cl}_4$; (2) with all the ammonia molecules united with the platinum, and the chlorine atoms attached to the nitrogen in certain ammonia molecules, and (3) with all the ammonia molecules and all the chlorine atoms united with the platinum.*

The second method of formulation has recently been adopted by Ramsay (Presidential Address, this vol., p. 786). Such formulae, however, would require isomerism due to differences in the points of

* A fourth arrangement has been recently suggested by Friend (this vol., 1009).

attachment of the chlorine atoms. Although the number of compounds with cationic complex which have been investigated is very large, no such case of isomerism appears to have been observed.

The third method of representation, with all the ammonia molecules and all the chlorine atoms united with the platinum, will therefore be used in the present paper. In this way, we obtain a formula containing a platinum atom, which is at least decavalent and which cannot be brought into agreement with Abegg's theory. Although it is not customary to assume valencies of such a high order as ten, there is no a priori objection to the use of even higher degrees of valency. Archibald and McIntosh have suggested that oxygen may be dodecavalent at very low temperatures (Trans., 1904, 85, 919).

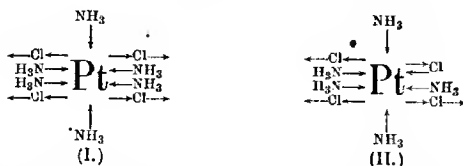
No attempt will be made in this paper to build up a new theory of valency. Indeed, in the opinion of the present author, a totally comprehensive and satisfactory theory of valency will not be possible until we have a much more complete knowledge of the constitution of molecular compounds, and also of the nature of chemical affinity, than we possess to-day.

In developing the following formulæ, it will merely be supposed, for the reasons given on p. 1565, that every element possesses two kinds of affinity, positive and negative. No assumptions will be made with reference to valency, or to the relative intensities of the affinities in question.

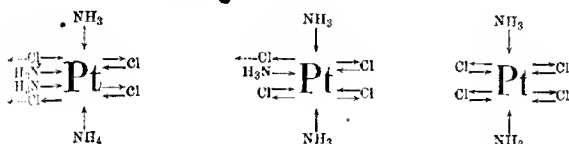
In the compound $(Pt6NH_3)Cl_4$, we then have a platinum atom with positive affinity, which is capable of combining with the negative affinity of four atoms of chlorine. The platinum atom also has negative affinity, which is combined in this compound with the free positive affinity of the nitrogen in six molecules of ammonia (compare the formula for ammonia on p. 1571). The chlorine atoms in the compound have positive affinity, which is unsaturated. In writing the following formulæ, the saturation of the affinities is represented by means of arrows pointing from positive to negative. Unsaturated affinity is represented by a dotted line with an arrow-head, pointing away from the atom if the affinity is positive and towards the atom when the affinity is negative. It does not necessarily follow that two affinities in combination as thus represented are completely saturated, since this can only occur when the affinities are exactly equal in amount but opposite in sign.

For $(Pt6NH_3)Cl_4$ we then have formula I. If a molecule of ammonia is removed from this formula, the platinum atom will have free negative affinity, which may be supposed to saturate the free positive affinity of one of the chlorine atoms, namely, the one which passes to the vacant place in the octahedron and loses its power

of ionisation. $(\text{Pt}5\text{NH}_3\text{Cl})\text{Cl}_3$ will then be represented as II. By



repeating the process, we obtain for the compounds $(\text{Pt}4\text{NH}_3\text{Cl}_2)\text{Cl}_2$, $(\text{Pt}3\text{NH}_3\text{Cl}_3)\text{Cl}$, and $(\text{Pt}2\text{NH}_3\text{Cl}_4)$ respectively the formulæ:



If a molecule of ammonia is removed from the substance $(\text{Pt}2\text{NH}_3\text{Cl}_4)$, there is no longer a chlorine atom with free positive affinity to saturate the negative affinity of the platinum atom which is thus liberated. An atom of chlorine in an ionisable chloride, such as $\rightarrow \text{K} \rightarrow \text{Cl} \rightarrow$, will, however, serve the same purpose, and for $(\text{PtNH}_3\text{Cl}_5)\text{K}$ and $(\text{PtCl}_6)\text{K}_2$ we obtain



The ionisable potassium atoms in these formulæ are written with free negative affinity. The affinity will, however, be very weak, as is evident from the absence of ammoniacal compounds of potassium salts and their tendency to crystallise from aqueous solutions in the anhydrous condition.

Dissociation.

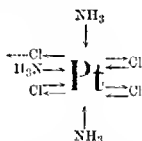
The dissociation in the above series of compounds takes place, according to Werner (*Zeitsch. anorg. Chem.*, 1893, 3, 325), owing to the action of the water molecules, which press in between the octahedron and the atoms outside it, thus forcing them apart. In the ideal case of a perfectly stable complex, a chlorine atom situated at the corner of the octahedron does not dissociate, because the water molecules are unable to penetrate the octahedron itself. In addition to this manner.

of dissociation, a study of the formulæ suggested above leads to the following considerations as factors in determining the extent to which a given chlorine atom will be ionised.

In a solution of an electrolyte, we have the following equilibria (compare Abegg, *Zeitsch. anorg. Chem.*, 1904, **39**, 359):

- (1) Ion + ion \rightleftharpoons undissociated compound.
- (2) Ion + solvent \rightleftharpoons compound of ion and solvent.
- (3) Undissociated compound + solvent \rightleftharpoons (compound of the same).

As an example, take the formula

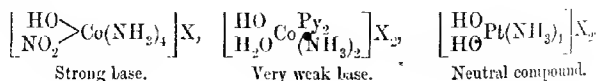


The three chlorine atoms situated in the octahedron are united to the platinum with two kinds of affinity instead of one, as is the case with the fourth chlorine. There will therefore be a much smaller tendency to dissociate, according to equation (1), on the part of the three chlorine atoms in the octahedron than on the part of the fourth, situated outside the octahedron.

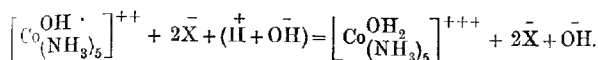
That the water molecule has free positive and also free negative affinity is evident from its tendency to polymerise in the liquid state. If therefore in a complex (MX_6) in aqueous solution an atom X has residual affinity, it will be attracted by the opposite affinity of the water molecules, and in virtue of this attraction will tend to leave the complex.

In a perfectly stable complex (MX_6), the positive affinity of X_6 would be exactly saturated by the negative affinity of M. If the positive affinity of X_6 were greater than the negative affinity of M (compare p. 1566), then the positive affinity of the X atoms would not be completely saturated, and they would have a tendency to dissociate from the complex as shown above. If, as a result of this tendency, an X atom were to leave the octahedron, its place would be taken by a molecule of the solvent in virtue of the mass action of the latter. If the solvent were water and the atom, which had left the complex, a chlorine atom, we should have the well-known transformation of a chloro-compound into an aquo-compound.

Quite recently Werner has described a series of hydroxo-compounds, which include substances of all degrees of basicity. From this interesting series, the following instances may be taken (*Ber.*, 1907, **40**, 4133):



The basicity of these compounds is caused, according to Werner, by the hydrogen ions of the water, which react in the manner indicated in the equation

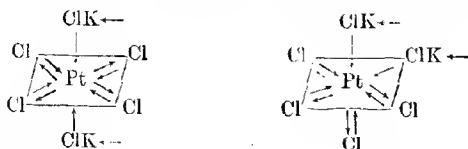


According to the above reasoning, the basicity might also result from a simple dissociation of the hydroxyl group from the complex, followed by the addition of water. In both explanations, the cause of the reaction is to be sought in the free positive affinity of the oxygen in the hydroxyl group. The greater this positive affinity the more easily would the hydroxyl leave the complex (as shown above). The free affinity would also provide the point of attack for the hydrogen ions in Werner's equation. The varying degrees of basicity of hydroxo-compounds can therefore be explained on the assumption that the oxygen atom of the hydroxyl group possesses free positive affinity, which is greatest in the compounds which are most strongly basic, and is zero in those which are perfectly neutral.

Isomerism.

In the compounds $(\text{Pt}6\text{NH}_3)\text{Cl}_4$ and $(\text{PtCl}_6)\text{K}_2$, according to the theory of co-ordination, the atoms outside the brackets are not combined with any particular atom or group at the corners of the octahedron, but with the complex as a whole. They will therefore take up some position of equilibrium outside the octahedron, and isomerism due to differences in this position is not to be expected. The same holds good for the formulæ suggested in this paper, so long as the complex is positive, because the ionisable atoms outside the octahedron are in union with the affinity of the central atom and not with atoms or groups at the corners.

When the complex is negative, the case is quite different. Take the formula which has been suggested for potassium platnichloride :

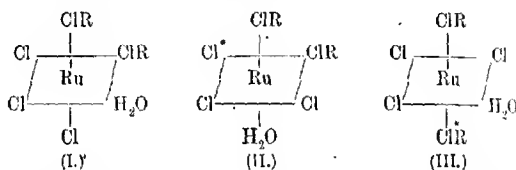


The potassium atoms in this formula are united with certain definite chlorine atoms in the complex. Isomerism should therefore be possible in the salts of complex acids, owing to variations in the positions of attachment of the positive atoms.

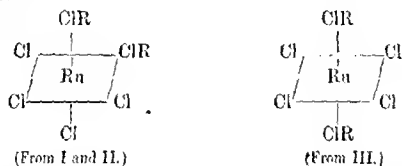
The following cases of isomerism in compounds with an anionic complex are taken from the list of unexplained instances of isomerism in Werner's recent work, "*Neuere Anschauungen auf dem Gebiete der anorganischen Chemie*," p. 189.

J. L. Howe (*J. Amer. Chem. Soc.*, 1901, 23, 775) has described compounds of the formula $(\text{RuCl}_5\text{H}_2\text{O})\text{R}_2$, which are different from the salts of the same composition prepared by Miolati and Tagini (*Gazzetta*, 1900, 30, ii, 511). When heated, they lose water and give substances of the formula $(\text{RuCl}_5)\text{R}_2$, which are distinct from the ordinary chlororuthenates. When treated in aqueous solution with chlorine, Howe's aquopentachlororuthenates give hexachlororuthenates, $(\text{RuCl}_6)\text{R}_2$, which are isomeric with the compounds of the same formula described by Antony and Lucchesi (*Gazzetta*, 1899, 29, ii, 82).

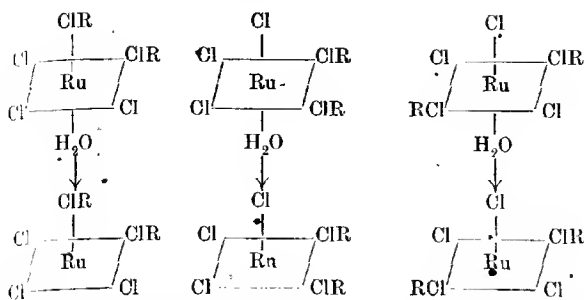
According to the formulæ developed in this paper, $(\text{RuCl}_5\text{H}_2\text{O})\text{R}_2$ should exist in the following three forms:



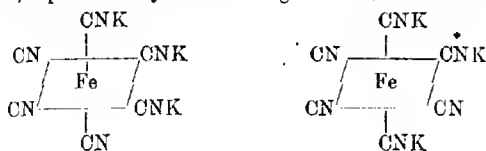
On chlorination, these three salts would give two hexachlororuthenates:



If the third aquopentachlororuthenate could be prepared and converted into the hexachlororuthenate, it would then be possible to determine the configuration of the hexachlororuthenates and of the aquopentachlororuthenate represented by formula III. On the loss of one molecule of water, the three compounds, $(\text{RuCl}_5\text{H}_2\text{O})\text{R}_2$, would give two, or perhaps three, salts of the composition $(\text{RuCl}_5)\text{R}_2$ in the following manner:



Locke and Edwards have prepared a modification of potassium ferricyanide which is different in chemical properties from the ordinary form (*Amer. Chem. J.*, 1899, 21, 193, 413). Theoretically, two isomerides, represented by the following formulae, should exist:



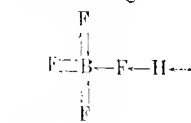
Conclusions.

The method of formulating co-ordinated compounds which has been described in this paper is perhaps worthy of consideration for the following reasons:

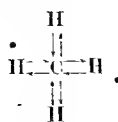
1. It affords a simple explanation of the changes in valency and in sign of the complex in a series of compounds like the platinum salts instanced above.
2. It suggests certain factors as being of importance in determining the extent to which an atom in a co-ordinated compound can be ionized in aqueous solution. These factors depend on the amount of free affinity possessed by such an atom.
3. It explains all the known cases of isomerism among compounds with an anionic complex.

The method of formulation can of course be applied to co-ordinated compounds in general, whatever co-ordination number the central atom may have.

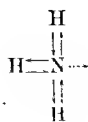
The following will serve as illustrations:



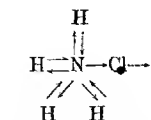
Hydrogen borofluoride.



Methane.



Ammonia.



Ammonium chloride.

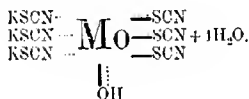


Potassium silicofluoride.

It will be observed that in all these formulae, ionisable atoms are represented with free affinity; non-ionisable atoms, on the contrary, have both kinds of affinity satisfied.

Addendum.

In a paper which has appeared since the above was written, Maas and Sand (*Ber.*, 1908, 41, 1500) have used similar formulae for representing co-ordinated compounds with anionic complex. They write $\text{K}_3[\text{Mo}(\text{SCN})_6\text{OH}] + 4\text{H}_2\text{O}$ as :



CLII.—The Rapid Electroanalytical Deposition and Separation of Metals. Part II. Antimony and Tin. The Employment of a Diaphragm.

By HENRY JULIUS SALOMON SAND.

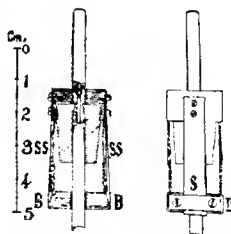
Apparatus.—The apparatus employed in the first part of this investigation (*Trans.*, 1907, 91, 374) has been modified only very slightly. The tripod has been normally placed on a few flat, wooden blocks or plates, so that when desired the beaker may be lowered relatively to the electrodes by removing the blocks. This is important when large quantities of liquid, such as those employed in the deposition of tin after removal of the antimony, are dealt with, and is also convenient in the process of washing-out. A new pair of electrodes has been obtained. The frame of both is made entirely of iridium-platinum, and the outer has been designed so that it may be held in as narrow a vessel as possible. It will pass through an opening of 34 mm. The stem of the inner electrode has been lengthened to 16 cm., and is not contracted at the top. The weights of the electrodes are 34.5 and 27.5 grams respectively. The chuck, *B* (Fig. 4,

loc. cit.), has been replaced by a specially-designed clutch, which is shown in section in Fig. 1*a*, and in elevation at right angles to Fig. 1*a* in Fig. 1*b*. In it the stem of the electrode is held by a rubber cork, which is fastened into the clutch without cement in the manner shown, and can easily be renewed when desired. Contact is made by two brass blocks, *BB*, which are suspended by two pieces of flexible wire and held against the stem by the two double springs, *SS*. They are faced with platinum foil. A vent-hole, *H*, allows the air at the top of the cork to escape. Apart from the fact that the connexion can be instantly undone, the advantages of this clutch are to be found in the platinum contacts, and in the fact that it may be employed with glass-stem electrodes, the description of which is reserved for future publication.

The use of a mercury contact in the tubes leading to the clutch holding the anode has been criticised by A. Fischer (*Zeitsch. Elektrochem.*, 1907, 13, 469) in a paper in which the results obtained for bismuth, in Part I of the present investigation, have been confirmed. To avoid it he makes the inner electrode stationary, and stirs with a special glass stirrer, an arrangement which appears to me to be inferior to mine in convenience of manipulation. With regard to mercury contacts, I have always been fully alive to their grave practical disadvantages where there is any possibility of spilling drops of mercury. Such a possibility, however, does not exist in the present case. The great advantage of mercury contacts in remaining practically free from electrical and mechanical resistance in the atmosphere of a chemical laboratory has led me deliberately to choose this form of connexion, a choice which has been fully justified by nearly three years' practical experience.

The description of the washing of the electrodes (p. 382, *loc. cit.*) has led to misapprehension in some quarters (Foerster, *Zeitsch. Elektrochem.*, 1908, 14, 7; see also p. 92); it therefore seems desirable to state explicitly that, after lowering the beaker in which the electrolysis was carried out and simultaneously washing the cathode with a jet of water from a wash-bottle, the beaker is replaced by an empty one and the electrodes are again washed with a few drops of water or very often disconnected without further washing. The total amount of water employed thus only amounts to a few c.c. It is only when the exhausted liquid is not required for further use that the electrodes are generally dipped into two successive beakers containing pure water.

FIG. 1.



The gravimetric estimation of antimony and tin, when present in the same substance, is still considered one of the most troublesome operations by most analysts.

Rapid methods of electroanalysis have hitherto met with but little success in the case of the metals antimony and tin. Exner (*J. Amer. Chem. Soc.*, 1903, 25, 896) gives some numbers for antimony, but there is nothing to show that he was using solutions of a known concentration. Working under very similar conditions, I have always found high results (*Zeitsch. Elektrochem.*, 1907, 13, 326). Better results may probably have been obtained by Langness and Smith (*J. Amer. Chem. Soc.*, 1905, 27, 1524). On the other hand, Scheen (*Zeitsch. Elektrochem.*, 1908, 14, 257), working in the Aachen laboratory under similar conditions, quite recently obtained high results. Tin was determined by Exner (*loc. cit.*) and by Medway (*Amer. J. Sci.*, 1904, 18, 56) in neutral oxalate solutions of stannous salts, and recently by Witmer (*J. Amer. Chem. Soc.*, 1907, 29, 473) both in stannous and stannic salts by the employment of an ammonium sulphide solution. No separation of the two metals by rapid methods has been attempted hitherto.

The Formation of Antimony Hydride.—The only solutions from which antimony has hitherto been deposited in a coherent form for analysis have been alkaline (solutions of sulpho-salts: Classen's method) or neutral (tartrate solutions: Law and F. M. Perkin, *Trans. Faraday Soc.*, 1905, 1, 251); acid solutions have always been believed to yield spongy deposits. The reason for this is to be sought in the intermediate formation of hydrides, a matter to which special attention has been drawn in Part I, particularly with regard to bismuth. These endothermic compounds are particularly liable to be formed at a low temperature, and in the presence of many hydrogen ions. In all cases their formation can be prevented by maintaining the potential of the cathode at a sufficiently low value and employing a high temperature. It has thus been possible in the present investigation to extend the application of electroanalysis to strongly acid solutions containing sulphuric acid, sometimes with the addition of chlorides. Perfectly coherent deposits of a light grey colour have thus always been obtained without sacrificing the great advantages which simple acid solutions always offer both for the determination and for the separation of metals (see Part I, p. 401; also Foerster, *Zeitsch. angew. Chem.*, 1906, 19, 1842, and Classen, *Zeitsch. Elektrochem.*, 1908, 14, 239). Solutions containing only oxalic and tartaric acids in the free state have also been shown to be capable of yielding perfectly coherent deposits under the conditions outlined. They are, however, unsuitable for separations, as they cannot be exhausted at a low potential.

The Reduction of Antimonic and Stannic Compounds.—Antimonic compounds must always be taken account of in the electroanalysis of solutions containing antimony, for they are almost invariably formed at the anode, at least in small quantity, even when the electrolyte originally contains only trivalent antimony. The reduction of these compounds must not be classed with the ionic reactions, but is comparable rather with the electrolytic reduction of dissolved non-electrolytes. In contrast to purely metallic salts, to which the compounds of trivalent antimony may, for purposes of electroanalysis, be said to belong, and which are reduced almost instantaneously and reversibly,* the reduction of antimonic compounds does not in general take place instantly at a definite potential, but is accomplished slowly, the rate depending on various influences, which may be classified under the heading "catalytic." In alkaline solution, it is in general exceedingly difficult to reduce them, although the sulpho-salts can be readily kept in the amphoteric state by the addition of potassium cyanide. Alkaline tartrate solutions, although yielding coherent deposits, cannot be conveniently exhausted of quinquevalent antimony, and are thus useless for purposes of rapid electroanalysis. The same applies to neutral solutions. In strongly acid solution, on the other hand, reduction takes place more readily. When a sulphuric acid solution or suspension has been electrolysed at an auxiliary potential† not exceeding 0.75 volt and at 100° for some time, the greater part of the antimony disappears from solution, but a small amount remains as antimonic salt for a very long time. In the presence of a small amount of hydrazine sulphate, the whole of the antimony disappears from solution slowly at an auxiliary potential of 0.75 volt, when the concentration of the acid is 1 part by volume of concentrated acid to 4 parts by volume of solution. When, on the other hand, the concentration of the acid is 1 part by volume to 1 part of water, and the temperature is maintained above 100°, the antimony disappears from solution completely in the presence of a small quantity of hydrazine sulphate at an auxiliary

* A cation would be deposited reversibly if the P.D. cathode-electrolyte were the same whether a current passes or not. In this case, the concentration of the cation in the layer of liquid touching the electrode would follow directly from the observed cathode-potential by Nernst's formula. According to Coffetti and Foerster's results (*Ber.*, 1905, 38, 2934), copper and other metals are deposited from acid solution at a potential very near that of equilibrium. I have also been engaged in the study of the reversibility of metal deposition for the last four years, but have not had time to complete my experiments. I find that, under certain conditions, copper may be deposited in a manner approaching "reversibility" still much nearer than follows from the results of these authors.

† The words "auxiliary potential" are used to express the difference of potential between the 2N-sulphuric acid auxiliary electrode and the cathode or outer electrode. See also Part I, note, p. 281.

potential of 0.65 volt with a rapidity which is quite sufficient for the purposes of rapid electroanalysis, and it is on this fact that the method given in the present paper is largely based. (For notes on the behaviour of hydrazine sulphate as a depolariser see p. 1580.)

The behaviour of the halogen compounds as catalysts is very striking. A very small amount of a chloride, bromide, or iodide* added to an antimony solution containing one-quarter of its volume of concentrated sulphuric acid causes the solution to be exhausted completely with great rapidity at a temperature of 100° and an auxiliary potential of 0.65 volt. For purposes of analysis, the only halide that need be considered is the chloride, as antimony has not been deposited from solutions containing bromine and iodine without inclusion of the halogen (see p. 1577). The behaviour of tin is very similar to that of antimony. Stannic compounds require a higher potential for their reduction than stannous,—from all solutions, except strongly acid ones containing chlorides. This can be very plainly demonstrated by electrolysing a solution containing about 0.5 gram of tin as stannic sulphate, some hydrazine sulphate, and approximately equal volumes of sulphuric acid and water at about 100° with platinum electrodes, and at an auxiliary potential of 0.65 volt. A small residual current of about 0.3 ampere will pass. On the addition of about a gram of sodium chloride, however, the current will suddenly rise to several amperes, owing to reduction of the stannic salt. When a cathode covered with antimony is employed, the phenomenon is still more marked.

In acid solutions containing chlorides, stannic salts are thus, in general, readily reduced to the stannous state, and it is only after either the whole or the greater part of the stannic compound has disappeared from solution that the potential will rise sufficiently to allow the further reduction of the stannous compound to metal to take place. If the stannous compound formed is oxidised back to the stannic state at the anode in quantities almost as great as those in which it is formed at the cathode, the greater part of the current is expended as a "residual" current in doing quite useless work (see Part I, p. 392). In solutions containing only free oxalic and sulphuric acids, on the other hand, the reduction of stannic compounds takes place at a much higher potential than that of the stannous, and thus reduction proceeds directly to the metal without the intermediate formation of stannous compound to a measurable extent. In certain cases, such solutions are thus very well suited for electroanalysis, and results are given in support of this. When, however

* Fluorides behave differently. Solutions of antimonous salts containing fluorides require a higher potential for their decomposition than those containing other halogen salts.

large quantities of salts, such as ammonium sulphate, are present, these hinder the reduction to such an extent that, in spite of the high super-tension of a tin-covered electrode, it becomes impossible to exhaust the solution in a reasonable period of time. In the present investigation, the solutions, from which the tin was deposited after the removal of the antimony, contained large quantities of ammonium sulphate. The expedient adopted was to deposit first in the presence only of sulphuric and oxalic acids. The greater part of the tin thus appears in a beautiful silvery form, corresponding with the high potential of the electrode (see Part I, p. 385), and a high supertension is ensured. At the same time, most of the oxalic acid is removed by oxidation at the anode. Hydrochloric acid and hydroxylamine hydrochloride are then added, by which the reduction of the remaining stannic compound is greatly facilitated, and the solution may be exhausted completely. The purpose of the hydroxylamine compound is to protect the anode from the nascent chlorine, which would otherwise be formed. This depolariser was first employed by Engels (*Zeitsch. Elektrochem.*, 1896, 2, 418).

• *The Simultaneous Precipitation of Non-electrolytes and Metals in its Relation to the Electro-deposition of Antimony.*—Electrolytic metal deposits are not infrequently found to contain small quantities of non-electrolytes, a circumstance which constitutes one of the most troublesome difficulties the electro-analyst has to meet. This phenomenon plays a specially important part in the case of antimony. From chloride, bromide, and iodide solutions, deposits are well known to be formed containing the halogen. It has been found in the present investigation, in agreement with Cohen and Ringer (*Zeitsch. physikal. Chem.*, 1904, 47, 1), that antimony may be deposited at boiling temperature free from chlorine in a solution containing small amounts of chloride. Iodine, on the other hand, appears to be always deposited with the metal when it is present in the solution.

From solutions of sulpho-salts, deposits are likewise frequently obtained containing impurities (compare Dormaar, *Zeitsch. anorg. Chem.*, 1907, 53, 349; Foerster and Wolf, *Zeitsch. Elektrochem.*, 1907, 13, 205; H. J. S. Sand, *Zeitsch. Elektrochem.*, 1907, 13, 326; Scheen, *Zeitsch. Elektrochem.*, 1908, 14, 257; Cohen, *Zeitsch. Elektrochem.*, 1908, 14, 301). This has led to the rejection of such solutions for purposes of the present investigation.

When moderately acid or alkaline stannic solutions are kept, they are well known to become turbid, owing to the formation of *b*-stannic acid. This compound will dissolve on warming with more acid, and on the addition of a stannous salt it produces a yellow coloration (Löwenthal, *Dumner's Handbuch*, Vol. II, Part I, p. 654). It has been found in the present investigation that a similar yellow compound

is formed when antimonous salts are present. If the antimony is deposited from such a solution at a potential below the deposition potential of tin, results are nevertheless obtained which are always considerably high, owing to the inclusion of tin. The deposit has not been analysed, but it appears almost certain that the tin is contained in it in the form of tin oxide. In several experiments in sulphuric acid solution, quantities of antimony varying between 0.36 and 0.45 gram were taken in conjunction with a solution of *b*-stannic acid corresponding with 0.28 to 0.35 gram of tin, and the results showed errors varying between 2 and 2.5 centigrams. When 0.3 gram of sodium chloride was added in one experiment in which 0.43 gram of antimony was taken in the presence of 0.35 gram of *b*-stannic acid, the antimony deposit weighed 0.52 gram. The formation of *b*-stannic acid must therefore be prevented, and it is necessary to work in a solution consisting largely of sulphuric acid in which *a*-stannic acid is stable. The concentration chosen was 1 part by volume of sulphuric acid to 1 part of water. When small amounts of tin only are present, the concentration of the acid may be slightly lower. If the solution to be analysed originally contained *b*-stannic acid, it becomes necessary to evaporate the water. In the concentrated acid left, the transformation from *b*- to *a*-stannic acid then takes place readily, and, on diluting, correct results are obtained.

In one experiment a considerable amount of oxalic acid was added. This, too, had the effect of causing precipitation of the tin, a result which requires further investigation for its explanation.

Numbers and other Experimental Details. Antimony.—All the experiments described were carried out with pure antimony (Kahlbaum), the impurities of which are quite negligible. As antimony is said to oxidise slowly in air (Ditte and Metzner, *Ann. Chim. Phys.*, 1893, [vi], 29, 389), it was always kept in an evacuated desiccator when in the powdered condition. Special experiments showed that it does not change in weight in these circumstances. The volume of the solution was in all experiments about 80 c.c.

Experiment 1.—The metal was dissolved in hot concentrated sulphuric acid (altogether 20 c.c.), and the cold solution diluted to 80 c.c. A considerable amount of antimony compound separates out of the solution under these conditions, but disappears again during the course of the experiment. The greater part of the deposition proceeds at the initial potential of the cathode, but to complete the reduction of the antimonous compound formed, the potential must be pushed to a fairly high value, and a considerable time is necessary.

Experiments 2, 3, and 4 were carried out in similar circumstances, except that hydrazine sulphate was added after the experiment had proceeded for about ten minutes to facilitate the reduction of antimonous

compound. Thus it was possible to complete the reduction at the lower auxiliary potentials given. The quantities of hydrazine sulphate were 1 gram in No. 2, 0.5 gram in No. 3, and 0.25 gram in No. 4.

No.	Sb taken.	Sb found.	Amps.	Volts, anode-cathode.	Volts, auxiliary.	Temp.	Time, mins.
1	0.2973	0.2973	3--0.6 then 0.8--1.0		0.55 0.80	100°	33
2	0.3635	0.3674	3--0.3		0.57--0.75	100	32
3	0.3708	0.3705	3--0.3		0.56--0.75	100--105	30
4	0.4316	0.4336 0.4349	3--0.3		0.56--0.70 0.75	100--105	30 + 10
5	0.3315	0.3321	3--0.2	0.8--0.5	0.57--0.65	97	17
6	0.3239	0.3242	3--0.2		0.60--0.65	98	15
7	0.4000	0.4001	5--0.2	1.3--0.6	0.57--0.65	100--103	15
8	0.4449	0.4452	5--0.2	2.1--0.5	0.57--0.65	100--105	20
9	0.3572	0.3573	4--0.4	1.8--0.7	0.54--0.65	105--110	15
10	0.1110	0.1110	2--0.3		0.57--0.65	100--110	15
11	0.3989	0.3977 0.3983	4--0.4	2.0--0.5	0.57--0.65	100--105	25 + 10
12	0.4194	0.4194	4--0.3	1.5--0.5	0.55--0.65	105--110	20
13	0.3487	0.3474	3--0.3	2.3--0.5	0.55--0.65	100--115	25
14	0.4043	0.4050	3.5--0.4	1.3--0.3	0.52--0.65	115--120	18
15	0.5035	0.5051	4--0.3	1--0.6	0.50--0.65	105--115	20
16	0.4018	0.4027	4--0.3	—	0.50--0.65	100--105	20
17	0.2108	0.2116	3--0.4	2--0.7	0.50--0.65	105--110	18

Experiments 5 and 6 were carried out in a solution containing chloride. The quantities of reagents were concentrated sulphuric acid 10 c.c., sodium chloride 2.5 grams, hydrazine sulphate 0.5 gram. The solution was perfectly clear from the beginning of the experiment. No change in weight of the anode took place.

In Nos. 7--10, after the experiment had proceeded for about ten minutes, hydrazine sulphate and 0.1 gram of sodium chloride were added in order to exhaust the liquid of antimony; the quantities of the former reagent were 0.6 gram in No. 7, 0.2 gram in No. 8, and 0.5 gram in Nos. 9 and 10. The quantities of concentrated sulphuric acid were 30 c.c. in Nos. 7 and 8, and 40 c.c. in Nos. 9 and 10. In the two last named, 10 grams of oxalic acid were added, as it was thought that this reagent might perhaps prove of value in separations (see, however, p. 1578).

Experiments 11--13 were completed at the low potential of 0.65 volt without the addition of chloride. The hydrazine sulphate (0.5--0.6 gram) was here added from the beginning of the experiment to hinder oxidation of the antimonous sulphate as much as possible. It was, however, found necessary to use no less than 30 c.c. of sulphuric acid per 80 c.c. of solution. In No. 11 the first result was obtained when only 20 c.c. were taken, the second being found after the addition of another 10 c.c.

Experiments 14—17 were carried out under the conditions which alone have proved suitable for separations from tin. The quantities of reagents were 40 c.c. of sulphuric acid, 40 c.c. of water, and 0.5 gram of hydrazine sulphate. In such a solution the reduction of any antimonious compound which may be formed proceeds very rapidly at a temperature above 100° , as has been proved by special experiments. There is reason to believe that a slight reduction of the sulphuric acid may take place, leading to the formation of sulphides and high results at temperatures above 120° and an auxiliary voltage of 0.65. It therefore seems advisable to maintain the temperature between 100° and 110° . No precipitates of antimony sulphate have separated from electrolytes having the composition of Nos. 14—17 even with the largest amounts taken (No. 49).

In all the experiments recorded, both the exhausted liquids and the wash waters have been tested for antimony, and no more than traces found.

As hydrazine sulphate plays an important part in all these determinations, the following notes on its behaviour as a depolariser may be given. Its efficiency appears to be slight when the current is started at a high value, and a difference of about 2 volts is generally observed between the anode and the cathode. When, however, the current is reduced, the depolarising action suddenly becomes much more powerful, and the voltmeter may suddenly drop from about 2 to a little more than half a volt. On again increasing the current, the voltage will remain at its low value until a very large increase of the current has taken place. Those facts must be borne in mind when the regulation of the current is interrupted for a short time in order to wash down the beaker or for similar reasons. If the voltage has then not fallen to its low value, it should always be made to do so by momentarily decreasing the current, as otherwise great variations of the latter might take place and possibly ruin the determination. When the anode has been moving very fast, crystals trapped between its stem and the guide-tube have occasionally led to the formation of a trace of a red substance around the stem, believed to be antimonious sulphide. An effect on the results has never been perceptible.

Tin.—In all the experiments, metallic tin (Kahlbaum), the impurities of which are negligible, was employed. A standard solution was made up by dissolving a known weight of scraped metal in hot concentrated sulphuric acid. A considerable amount of sulphur was produced, and a small quantity of tin oxide was left undissolved. After diluting, the solution was filtered, the tin oxide weighed, and a correction made for it (almost negligible). The solution contained 100 c.c. of concentrated sulphuric acid per litre, and was perfectly clear when first made up. On keeping, it gradually became opalescent and then milky, owing to

the formation of *b*-stannic compound. At the time the experiments tabulated were carried out, no precipitate separated out, so that it was possible to use a pipette to measure the solution.

In all the experiments, the liquid was first made neutral, or only slightly acid to methyl-orange, by means of concentrated ammonium hydroxide, and oxalic acid was then added to dissolve the stannic hydroxide formed.

No.	Age of solution, days.	Sn taken.	Sn found.	Amps.	Temp.	Time, mins.	Constant to mg.
18	3	0.3500	0.3497	3	70—100°	40	0.4
19	5	0.2797	0.2802	10	85	10	—
20	6	0.2797	0.2760	5	70	23	—
			0.2809	10	90	+5	0.4
21	7	0.2797	0.2804	5	70—80	20	—
			0.2812			+18	0.8
22	8	0.3500	0.3497	5	70—80	38	-0.3
23	13	0.0023	0.0023	3	95	9	—
24	13	0.0023	0.0027	3	100	8	—
25	14	0.3500	0.3496	5—2	98	20	0.4
26	15	0.3500	0.3494	4—2	90—99	29	-0.8
27	15	0.3500	0.3503	5—2	80—99	15	-0.2

As there is no reaction by which a solution containing oxalic acid can be readily tested for traces of tin, the deposits must be taken to constant weight. A special column of the table is devoted to the degree of constancy in milligrams obtained before the final weighing. To test a solution containing oxalic acid roughly for tin, it may be boiled for a few minutes with ammonium carbonate, which will lead to the formation of a precipitate or turbidity if the concentration of the tin is not exceedingly small.

The general conclusions drawn from the series of experiments are: firstly, that there should always be free oxalic acid present. As this reagent is oxidised rapidly at the anode, theoretically at the rate of 2.35 grams of crystals per ampere-hour, it should be replaced in sufficient quantity to allow 1 to 3 grams per 80 c.c. of solution to be present at the end. Secondly, in order to secure rapid deposition of the tin, 0.1 to 0.2 c.c. of concentrated sulphuric acid should be present in the free state before the addition of the oxalic acid. Thirdly, a temperature near the boiling point should be maintained. A current of about 3 to 5 amperes may be used at the beginning of the experiment, and be reduced to 2 amperes at the end. In the experiments in which 10 amperes were employed, the deposit was loose. The conditions laid down here were not strictly adhered to in all the experiments. It appeared easier to deposit all the tin when the solution was new than later on, when a considerable amount of *b*-stannic compound had been formed. The age of the solution at the time each experiment

was carried out is stated. The amounts of oxalic acid crystals employed were 2.3 grams in No. 18, 5 grams in Nos. 19 and 20, 3 grams in Nos. 21—23, 4 grams in No. 24, 3 grams at the beginning and 2 grams after ten minutes in No. 25, and 5 grams in Nos. 26 and 27. In most of the experiments, the solution was made just acid to methyl-orange before the addition of the oxalic acid. In excess of this, 0.1 to 0.2 c.c. of concentrated sulphuric acid was introduced in Nos. 25—27. The voltage varied from under 2 to almost 4, according to the conditions of the experiment, and the auxiliary electrode usually rose from about 0.9 to 1.3 volts during an experiment. (For the deposition of tin from solutions containing large quantities of ammonium salts, see p. 1586).

Separation of Antimony from Tin.—It has been shown that antimony can readily be completely deposited in the presence of hydrazine sulphate from its solution in sulphuric acid (1:1) at an auxiliary potential of 0.65 volt and at temperatures above 100°. Tin does not begin to separate under similar conditions below 0.8 volt, and there should thus be no difficulty in effecting a separation. That difficulties are nevertheless met with when *b*-stannic compounds are present has already been stated. The following experiments, 28 and 29, show that these difficulties can be readily overcome if the water is evaporated from the solution and the latter then heated until copious, white fumes of sulphuric acid are produced:

No.	Sb. taken.	Sb. found.	Sn taken.	Age, days.	Amps.	Volts, auxiliary.	Temp.	Time, mins.
28	0.4539	0.4533	0.35	53	$\left\{ \begin{array}{l} 4-0.4 \\ 1-0.8 \end{array} \right\}$	0.57—0.35	105—110°	15
29	0.4469	0.4470	0.35	89	$\left\{ \begin{array}{l} 4-0.4 \\ 2.5-1 \end{array} \right\}$	0.57—0.65	105—110	18

In the fifth column, the age of the stannic solution is given. A considerable precipitate had separated out of the stock solution in No. 29; the quantities of tin are approximate. After ten minutes, 0.1 gram of sodium chloride was added, which caused the residual current to rise from the first to the second values given in the table. This was done in order to exhaust the solution of antimonic compound, but, as it was afterwards proved to be unnecessary and a large residual current is apt to lead to high results when the analysis is prolonged unnecessarily, the practice of adding chloride was entirely discontinued in later experiments.

In the following experiments, the ultimate object was to start from the pure metals and also to obtain a solvent which would dissolve such alloys containing antimony and tin as are likely to occur in chemical analysis. It was also thought desirable that the solvent should be capable of dealing with a precipitate of antimony and tin sulphides on

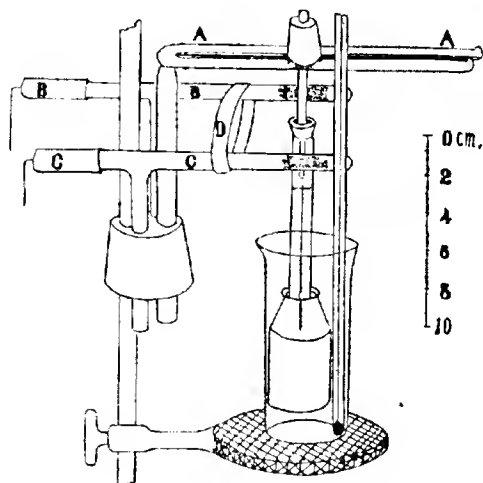
a filter-paper. Such a precipitate can obviously not be dissolved in sulphuric acid solution of the concentration required (1 : 1) without dissolution of filter-paper. If concentrated acid is taken, the latter will char, but not be completely destroyed within a reasonable time on subsequent heating unless a little nitric acid is added. It is not possible, as might be thought, to dissolve the precipitate in alkali sulphide solution, evaporate to dryness, and then treat the residue with sulphuric acid. Owing to the formation of alkali sulphate, hydrolysis of the stannic sulphate is brought about in such circumstances, which leads to the formation of a precipitate during subsequent electrolysis, and this would hinder a separation. It is equally necessary to add nitric acid when alloys containing tin and other electropositive metals form the starting point, as it is otherwise impossible to avoid the formation of sulphur, which cannot be removed completely without troublesome filtrations. Besides, some metals, such as copper, cannot be dissolved quantitatively in sulphuric acid unless a little nitric acid and water are present.

When nitric acid is added, nitrosulphonic acid is always produced from secondary causes. The latter, as is well known, cannot be removed by distillation, and, on diluting, nitrous and nitric acids are formed. On subsequent heating, a precipitate of antimony pentoxide separates out, which would cause a great deal of uncertainty in separations. If present in large quantity, it might be exceedingly difficult to reduce completely, and there is experimental evidence that when present in comparatively small quantity it may lead to high results, as it may separate out on the cathode partly unchanged from its supersaturated solution. It therefore becomes necessary to devise a method which will allow the complete destruction of the nitrosulphonic acid, the elimination of the nitric acid by distillation, and the reduction of any antimonious compound that may be formed during the process of solution. It was found impossible to destroy the nitrosulphonic acid quantitatively within a reasonable time by passing sulphur dioxide at a high temperature into the sulphuric acid solution containing a little water. Much more success was obtained by generating the sulphur dioxide electrolytically within the solution, but even so, antimony pentoxide was formed on diluting. The nitrosulphonic acid was found to be completely destroyed, and the antimony pentoxide reduced by the employment of hydrazine sulphate in a solution containing a little water. At first, the metal was dissolved in a beaker covered with a watch-glass, but drops of nitric acid always condense on the latter in the subsequent operations, and it is impossible to get rid of all of them completely. Finally, the procedure about to be described and illustrated in Fig. 2 was adopted.

The usual pattern of beaker was employed, namely, one approx-

imately 42 mm. in diameter and 10 cm. in height. The electrodes were suspended in it in the acid about 1 cm. from the bottom and connected to the source of current, a thermometer being placed beside them. It is obviously necessary that no other materials than glass, platinum, and rubber should be present above and near the beaker. The stem of the inner electrode is pushed through a rubber cork and then slid into the glass fork *A*. The outer electrode is held in position by means of the guide-tube. Contact is made by the leads *B* and *C*. These consist of glass T-pieces, into the ends of which strips of platinum gauze have been fused. They are filled with mercury and closed at the ends by rubber caps made from pieces of rubber tube and solid

FIG. 2.



rubber cut from a cork. A copper wire passes through these. Particular attention may perhaps be drawn to the use of platinum gauze in making electrical connexions through glass for use with heavy currents. This mode of connexion was employed successfully in the apparatus Figs. 2 and 3, Part I, and also in the apparatus Fig. 3 in this paper. The connexions are easily made by cutting the glass tube at the place where the gauze is to be introduced, then widening out the edges of both pieces, putting the gauze in position, and then sealing the tubes together again. The pieces *B* and *C* are held against the stem and the collar of the electrode respectively by the rubber band *D*. The mode of holding *A*, *B*, *C* in a rubber cork

which slides on the rod of the retort stand will be understood from the figure. The apparatus was always used in a draught cupboard, and placed in an earthenware trough as a protection in case of accident to the beaker.

The acid employed consists of a mixture of 40 c.c. of concentrated sulphuric acid, 5 c.c. of water, and 2 c.c. of concentrated nitric acid. When this is heated to about 180°, solution of the metal usually takes place, and is completed fairly rapidly, the temperature being taken to about 220°. A current of 5 amperes is now passed. When the liquid has been heated to about 250–270°, vigorous effervescence takes place, which stirs it, and rapid reduction of the nitrosulphonic acid takes place. After the current has been passing at the high temperature for about five to ten minutes, it is stopped, and the liquid allowed to cool for at least ten minutes by about 100°. A quantity of hydrazine sulphate, generally equal in weight to the total amount of metal present and equal to 0.5 gram when the latter is below this, is now introduced. The liquid may be stirred by rotating the inner electrode, and is again heated. It is necessary to allow the electrolyte to cool down from 250° before introducing the hydrazine sulphate, as the decomposition of the latter at the high temperature would be so rapid that a great part of the liquid might escape any action whatever. The temperature is finally raised to 300°. When comparatively large quantities of antimony were present, a turbidity was sometimes formed during the operation, but this always disappeared later on. The gauze of the electrodes forms an efficient protection against loss by spitting. This has been repeatedly controlled by placing clock-glasses over the beaker, and afterwards testing the drops of acid which condense on them by hydrogen sulphide. In no case was any metal detected. When the temperature of the acid has fallen to about 100°, the beaker is placed first in warm and then in cold water. When it has thus been cooled to about 30°, 40 c.c. of water and a quantity of hydrazine sulphate, either approximately equal to that of the antimony or equal to 0.5 gram when the antimony was less than this value, are added. On careful stirring, the temperature rises to about 120°, and the analysis may be commenced. The above method has in every case been found trustworthy. No such reagents as diphenylamine should be added to test for nitrosulphonic acid, as they may cause high results.

The following experiments, 30 to 32, refer to antimony treated in this way :

No.	Sb taken.	Sb found.	Amps.	Volts, auxiliary.	Temp.	Time.
30	0.3281	0.3288	4–0.4	0.53–0.65	120–110°	
31	0.4025	0.4027	4–0.4	0.56–0.65	115	18
32	0.1383	0.1388	3–0.6	0.56–0.65	125–110	10

When tin is to be determined in the electrolyte freed from antimony

the sulphuric acid must first be neutralised with strong ammonia. This may be accomplished without loss in the following way: A 400 c.c. beaker of tall pattern and a clock-glass to cover it completely are obtained, and a hole drilled in the latter just large enough to allow the stem of the inner electrode to pass through it easily. The acid solution having been washed into the beaker, the oxalic acid is added, and the inner electrode placed in it; it is then covered by the clock-glass, and put in cold water in a trough under a hood. One hundred c.c. of concentrated ammonium hydroxide, namely, two and a-half times the volume of sulphuric acid, are now gradually poured on the top of the clock-glass, and the liquid simultaneously stirred by the inner electrode. As the ammonia runs down the stem of the electrode, vigorous ebullition takes place, especially at the beginning, but the beaker being completely covered, there is no possibility of loss. The clock-glass may now be washed and removed. A few drops of methyl-orange having been added—litmus must not be taken, as this colloid appears to hinder the subsequent precipitation of the tin—the liquid can be made neutral without fear of loss either by concentrated ammonia or sulphuric acid (1 : 4). It is now acidified, and an excess of sulphuric acid is added, corresponding with about 0.5 to 0.75 c.c. per gram of oxalic acid previously taken. It is preferable, although not absolutely necessary, to add the oxalic acid as described before neutralisation, and thus avoid the formation of a precipitate of stannic hydroxide.

The solution is now ready for electrolysis. A current of 4 amperes and a temperature of about 70° are usually employed for a length of time sufficient to destroy most of the oxalic acid. A much higher temperature cannot be taken conveniently, as the liquid sprays very much. During this time, most of the tin will have been deposited. The current is now interrupted, 15 c.c. of concentrated hydrochloric acid and 3 grams of hydroxylamine hydrochloride are added, and the temperature simultaneously raised rapidly to almost 100°. The electrolysis is then continued with a current of 3 amperes, which may afterwards be lowered to 2. In experiments 33–38, tin alone was taken. Nos. 39–48 constitute a complete series, in which both antimony and tin were employed. The amount of oxalic acid was 5 grams in all experiments, except No. 47, where 3 grams were considered sufficient. The time allowed to elapse before the addition

No.	Sn taken.	Sn found.	Amps.	Temp.	Time, mins.
33	0.5319	0.5315	4	70°; 90–95°	60
34	0.4891	0.4899	3	70°; 80°	60
35	0.5186	0.5178	3	60; 99	65
		0.5181			+ 14
36	0.9659	0.9679	4	70; 98	80
37	0.4721	0.4719	1	80; 97	70
38	1.0570	1.0596	4	80; 100	80

of the hydrochloric acid varied between seventeen minutes in No. 45 and thirty minutes in Nos. 36, 37, 42, 43, and 44. The amount of hydroxylamine hydrochloride added was usually 2 grams; it was raised to 3 as recommended above only in experiments 45 and 48. This was done as the anode was found to have been attacked slightly in some determinations. The latter was always weighed before and after each analysis, and was usually found quite or almost unchanged. It is obviously of the greatest importance that the anode should not be attacked, especially at the end of the experiments, as this would lead to deposition of platinum on the cathode and ultimately to complete destruction of the supertension of the latter, on which the success of the determination largely depends. As the anode is not under control, it is desirable to allow a considerable margin of safety, and it is with this end in view that the conditions given above were detailed. The second number given under the heading "temperature" is the value to which the latter was raised after the addition of the hydrochloric acid. It will be seen that in some cases it did not attain to approximately 100°. Similarly, the current was not reduced at the end in the majority of experiments as recommended. The weight of the deposit was, in nearly all cases, taken to constancy, and it is especially important in doing so to see that the temperature is raised sufficiently and the stirrer moving before the current is passed, as immediate attack of the anode by chlorine will take place if the depolariser is inefficient owing to a too low temperature, or has been exhausted at the electrode through lack of stirring. The greater part of the hydroxylamine is always found unchanged after an experiment, a circumstance which has been ascribed by Engels (*loc. cit.*) to the fact that the hydroxylamine is regenerated at the cathode after oxidation at the anode. This view appears to be correct, for I have always found nitric acid in small quantity in the electrolyte at the end of an experiment, and it is known that nitric acid may be reduced to hydroxylamine at a tin cathode. The auxiliary electrode usually showed about 1.5 volts at the beginning of an experiment and fell to about 1.3, sometimes even to about 1.15, volts at the end. In one case (No. 44), it ultimately fell to 1.07 volts, whereupon the experiment was interrupted and a slightly low result obtained. At the same time, the anode had decreased by more than a milligram. The anode and cathode showed a difference varying between 2 and 3 volts. Owing to the large amount of sulphuric acid employed, it is necessary to examine it specially for impurities. The acid employed in the present investigation contained 3.1 milligrams of lead and slightly less than 1 milligram of iron per 40 c.c. As special experiments have shown that the former metal is deposited completely with tin, 3.1 milligrams

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have been added to the amounts actually weighed out in the column "tin taken." No correction has been made for the latter metal. An uncertainty of a few tenths of a milligram is hereby introduced.

No.	Taken.	Fonnl.	Amps.	Volts, auxiliary.	Temp.*	Time, mins.
39	0.1146Sb	0.1153Sb	3-0.6	0.57-0.65	110-120°	20
	0.4652Sn	0.4649Sn	4	—	78°; 85°	69
40	0.1919Sb	0.1903Sb	3-0.4	0.56-0.65	110-120°	—
	0.4858Sn	0.4845 } Sn 0.4861 }	4	—	78°; 85°	69 +30 f
41	0.2433Sb	0.2438Sb	4-0.5	0.56-0.67	110-120°	20
	0.5008Sn	0.5006Sn	4	—	60°; 78°	69
42	0.0523Sb	0.0538Sb	2-0.4	0.55-0.67	110-123°	15
	0.5125Sn	0.5143Sn	4	—	80°; 93°	65
43	0.0963Sb	0.0984Sb	3-0.4	0.55-0.65	115-122°	22
	0.8541Sn	0.8555Sn	4	—	80°; 90°	89
44	0.1115Sb	0.1120Sb	3-0.5	0.57-0.65	110-118°	15
	0.8867Sn	0.8848Sn	4	—	75°; 90°	85
45	0.0997Sb	0.1010Sb	3-0.4	0.57-0.67	100-122°	20
	0.8691Sn	0.8691Sn	4; 3	—	80°; 93°	57
46	0.5062Sb	0.5064Sb	4-0.4	0.54-0.65	115-120°	25
	0.5353Sn	0.5369Sn	4; 3	—	75°; 97°	64
47	0.8722Sb	0.8705Sb	4-0.4	0.54-0.67	107-120°	25
	0.1580Sn	0.1583Sn	3; 2.5	—	65°; 97°	42
48	0.0931Sb	0.0947Sb	2.5-0.4	0.55-0.65	105-124°	15
	0.8508Sn	0.8511Sn	4; 2	—	76°; 96°	89

*The temperatures for tin are average values; the first refers to the experiment before the addition of hydrochloric acid and hydroxylamine hydrochloride, the other after.

It is well known that it is difficult to remove tin completely from a platinum cathode, and at the same time it is obviously necessary to do so before employing the latter for the determination of antimony. Perfectly satisfactory results were, however, obtained by first removing the metal with boiling hydrochloric acid and then heating the electrode to 250° in sulphuric acid to which a little fuming nitric acid had been originally added, or through which nitrogen dioxide had been bubbled.

In experiments 39-48, the pure metals were weighed out and dissolved together in the same beaker, as already described. In No. 46 the acid became very turbid, owing to the large quantity of antimony, but cleared again later on. The deposited antimony was tested for freedom from tin in experiments 39 and 44 by re-dissolving and re-depositing it. In the former case, a decrease of 0.6 milligram, in the latter an increase of 0.3 milligram, took place. There is a general tendency for the results for antimony to be high. No. 39 must be considered accidental, as the alcohol for drying was not at hand in this experiment. This tendency would probably have been remedied if lower temperatures had been employed (see p. 1580). In all cases, the time was more than what was deemed sufficient for complete deposition.

Separation of Antimony and Tin from other Metals.—The separation

of antimony and tin from other metals, especially from copper and lead, is of considerable practical importance, and a purely electrolytic method would probably offer great advantages. Most of the single separations involved have already been carried out; thus copper has been separated from antimony, antimony from lead, and lead from tin. The results, however, require confirmation and further elaboration, and are reserved for future publication.

The Use of a Diaphragm in Rapid Electroanalysis.

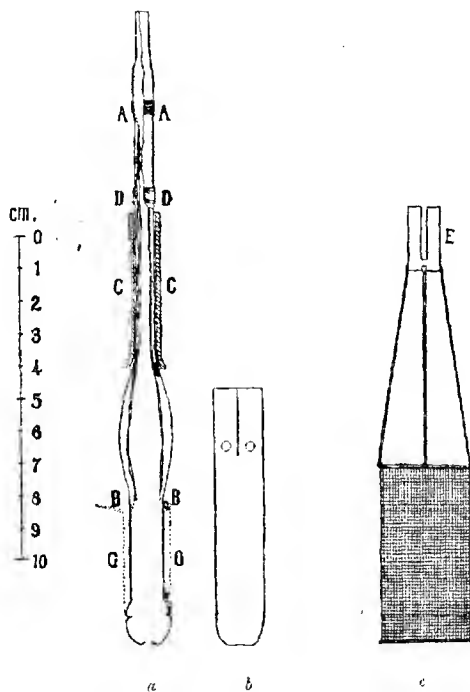
The fact that the processes taking place at the anode may frequently cause considerable difficulties has already been referred to on several occasions, and in some cases they may render an otherwise suitable electrolyte totally unfit for analysis. It was believed that particularly great difficulties would be met with in the case of tin, all preliminary experiments having been carried out in chlorido solutions. As has been seen, these difficulties may be met by the use of other solutions, and a diaphragm has therefore not been employed. Nevertheless, I believe that a brief description of the following apparatus, which was designed at the beginning of the present investigation, may be of interest, as it undoubtedly greatly extends the range of solutions available for electroanalysis, and may therefore acquire some importance in the future. A diaphragm with stationary electrodes was employed by Ost and Klapprot (*Zeitsch. angew. Chem.*, 1900, **13**, 828), but their apparatus is based on the assumption that none of the catholyte should find its way into the anode chamber.

In designing the present apparatus, it was thought that such an assumption could not in general be made, as diffusion will take place in all, but quite exceptional, circumstances. It was therefore decided that the apparatus should be made so that the whole of the anolyte could be washed into the cathode compartment after most of the metal was deposited.

Fig. 3a shows the anode. It is made mainly of glass, is open at the top, and has a hole at the bottom. Two strips of wire gauze connected to four platinum wires are fused through the glass at *A* in the manner described on p. 1584. On the outside, the gauze is bound over by platinum wire, against which contact may be made by the platinum-faced blocks, *H*, of the holder (Fig. 4). At *B* (Fig. 3a), the wires again emerge from the electrode by means of strips of gauze, and the latter are welded to strips attached to the gauze, *G*, forming the anode proper. The left side of the figure shows the strips after welding their ends, and the right after rolling up and tying down with platinum wire. The gauze *G* stands off from the glass a little to allow the gas bubbles generated in the heavy liquid to be thrown inwards, owing to centri-

fugal force, and thus escape. The rotating diaphragm (Fig. 3*b*) is cut from a Schleicher and Schüll parchment paper diffusion-shell. It is slit at the top to allow it to be tied round the top of the anode, and four holes have been punched into it through which to force the anolyte into the cathode chamber at the end of an experiment. The anode rotates in the guide-tube *C*, over which the collar, *E*,

FIG. 3.



of the cathode (Fig. 3*c*) slips. A piece of rubber tube, *D*, tied down with platinum wire, hinders the guide-tube from being pulled off with the cathode when the apparatus is being disconnected. *C* and *E* are held in a clamp in the same way as the ordinary electrodes.

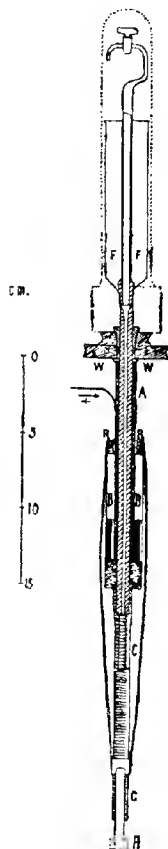
The holder of the anode is shown in Fig. 4. The current is introduced into the tube *A* made of gas-pipe, which is attached to the stand by an insulated cork held in a clamp. In this tube, the capillary plug funnel, *F*, rotates, a set of pulleys running on

the washer, *W*, being fastened to the capillary stem in the manner shown. Near the foot of the capillary tube, a cork is fixed holding the wide piece of bicycle tube, *B*, to which connexion is made from *A* by mercury. A cork ring, *R*, makes loss by splashing of the latter impossible. The capillary is finally extended in the rubber tube, *C*, into which the anode can be fastened. Near the end a brass ring is pulled over it, to which flexible wires making the connexion with *B*, and springs making the connexion with the blocks *H*, are soldered.

Before an experiment, the funnel is filled with the anolyte, and when the apparatus has been put together about 10 c.c. are allowed to run down to fill the anode compartment. At the end of an experiment, more liquid can again be run out by raising the plug, and the anolyte can thus be washed into the cathode chamber. The plug is made hollow, and a tap is fitted to it, so that it may be possible to blow liquid out of the interior of the hollow anode to which it has penetrated after interrupting an experiment. The dotted lines show a wide test-tube used to protect the funnel from dust when not in use, and a cork platform on which it rests.

In conclusion, records of a few copper determinations may be given which were carried out with this apparatus. The catholyte was of the ordinary composition, containing in Nos. 1 and 2, 1 c.c. of nitric acid, and in No. 3, 1 c.c. of concentrated sulphuric acid. The iron was added in the form of ferric alum, and was reduced to the ferrous state during the determination. No. 3 is an instance of a determination carried out under conditions which would have been very difficult, if not impossible, without the use of a diaphragm. The anolyte consisted of a molar solution of sodium hydrogen sulphate. The maximum voltage was

FIG. 4.



No.	Cu taken.	Cu found.	Fe taken.	Amps.	Volts, auxiliary, maximum.	Temp., approximately.	Time, mins.
1	0.2353	0.2354	0	6-1	-	50°	8
2	0.2353	0.2355	0	6-0.6	0.55	60	10
3	0.0118	0.0119	0.37	6-0.4	0.55	60	6

slightly more than four. The cathode in these three determinations was made of copper, whereas the one shown in the diagram is of platinum.

Part of the expense of this investigation has again been met by a Government Grant, for which the author desires to express his indebtedness.

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PART II.

973	17, col. 1	for "Georg" read "Wilhelm."
973	20, col. 1	" " " "

* From bottom.

of antimony and tin from other metals, especially from copper and lead, is of considerable practical importance, and a purely electrolytic method would probably offer great advantages. Most of the single separations involved have already been carried out; thus copper has been separated from antimony, antimony from lead, and lead from tin. The results, however, require confirmation and further elaboration, and are reserved for future publication.

The Use of a Diaphragm in Rapid Electroanalysis.

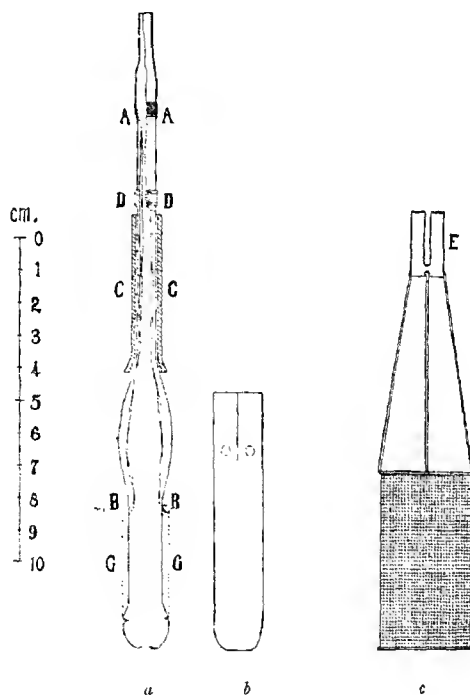
The fact that the processes taking place at the anode may frequently cause considerable difficulties has already been referred to on several occasions, and in some cases they may render an otherwise suitable electrolyte totally unfit for analysis. It was believed that particularly great difficulties would be met with in the case of tin, all preliminary experiments having been carried out in chloride solutions. As has been seen, these difficulties may be met by the use of other solutions, and a diaphragm has therefore not been employed. Nevertheless, I believe that a brief description of the following apparatus, which was designed at the beginning of the present investigation, may be of interest, as it undoubtedly greatly extends the range of solutions available for electroanalysis, and may therefore acquire some importance in the future. A diaphragm with stationary electrodes was employed by Ost and Klapprot (*Zeitsch. angew. Chem.*, 1900, 13, 828), but their apparatus is based on the assumption that none of the catholyte should find its way into the anode chamber.

In designing the present apparatus, it was thought that such an assumption could not in general be made, as diffusion will take place in all, but quite exceptional, circumstances. It was therefore decided that the apparatus should be made so that the whole of the anolyte could be washed into the cathode compartment after most of the metal was deposited.

Fig. 3a shows the anode. It is made mainly of glass, is open at the top, and has a hole at the bottom. Two strips of wire gauze connected to four platinum wires are fused through the glass at *A* in the manner described on p. 1584. On the outside, the gauze is bound over by platinum wire, against which contact may be made by the platinum-faced blocks, *H*, of the holder (Fig. 4). At *B* (Fig. 3a), the wires again emerge from the electrode by means of strips of gauze, and the latter are welded to strips attached to the gauze, *G*, forming the anode proper. The left side of the figure shows the strips after welding their ends, and the right after rolling up and tying down with platinum wire. The gauze *G* stands off from the glass a little to allow the gas bubbles generated in the heavy liquid to be thrown inwards, owing to centri-

fugal force, and thus escape. The rotating diaphragm (Fig. 3*b*) is cut from a Schleicher and Schüll parchment paper diffusion-shell. It is slit at the top to allow it to be tied round the top of the anode, and four holes have been punched into it through which to force the anolyte into the cathode chamber at the end of an experiment. The anode rotates in the guide-tube *C*, over which the collar, *E*,

FIG. 3.



of the cathode (Fig. 3*c*) slips. A piece of rubber tube, *D*, tied down with platinum wire, hinders the guide-tube from being pulled off with the cathode when the apparatus is being disconnected. *C* and *E* are held in a clamp in the same way as the ordinary electrodes.

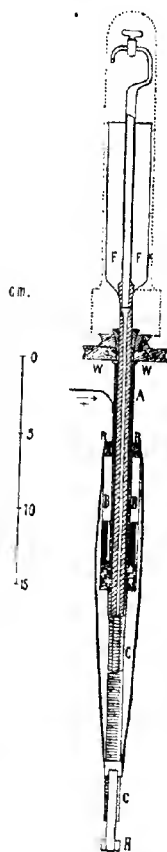
The holder of the anode is shown in Fig. 4. The current is introduced into the tube *A* made of gas-pipe, which is attached to the stand by an insulated cork held in a clamp. In this tube, the capillary plug funnel, *F*, rotates, a set of pulleys running on

the washer, *W*, being fastened to the capillary stem in the manner shown. Near the foot of the capillary tube, a cork is fixed holding the wide piece of bicycle tube, *B*, to which connexion is made from *A* by mercury. A cork ring, *R*, makes loss by splashing of the latter impossible. The capillary is finally extended in the rubber tube, *C*, into which the anode can be fastened. Near the end a brass ring is pulled over it, to which flexible wires making the connexion with *B*, and springs making the connexion with the blocks *H*, are soldered.

Before an experiment, the funnel is filled with the anolyte, and when the apparatus has been put together about 10 c.c. are allowed to run down to fill the anode compartment. At the end of an experiment, more liquid can again be run out by raising the plug, and the anolyte can thus be washed into the cathode chamber. The plug is made hollow, and a tap is fitted to it, so that it may be possible to blow liquid out of the interior of the hollow anode to which it has penetrated after interrupting an experiment. The dotted lines show a wide test-tube used to protect the funnel from dust when not in use, and a cork platform on which it rests.

In conclusion, records of a few copper determinations may be given which were carried out with this apparatus. The catholyte was of the ordinary composition, containing in Nos. 1 and 2, 1 c.c. of nitric acid, and in No. 3, 1 c.c. of concentrated sulphuric acid. The iron was added in the form of ferric alum, and was reduced to the ferrous state during the determination. No. 3 is an instance of a determination carried out under conditions which would have been very difficult, if not impossible, without the use of a diaphragm. The anolyte consisted of a molar solution of sodium hydrogen sulphate. The maximum voltage was

FIG. 4.



No.	Cu taken.	Cu found.	Fe taken.	Amps.	Volts, auxiliary, maximum.	Temp., approximately.	Time, mins.
1	0.2353	0.2354	0	6.4	—	50°	8
2	0.2353	0.2355	0	6-0.6	0.55	60	10
3	0.0118	0.0119	0.37	6-0.4	0.55	60	6

slightly more than four. The cathode in these three determinations was made of copper, whereas the one shown in the diagram is of platinum.

Part of the expense of this investigation has again been met by a Government Grant, for which the author desires to express his indebtedness.

UNIVERSITY COLLEGE,
NOTTINGHAM.

(CLIII).—*The Electrolytic Chlorination of the Salts of Organic Acids.*

By JOHN KENNETH HAROLD INGLIS and FRED WOOTTON.

ALTHOUGH electrolytic methods are now often of commercial importance, very little is known regarding the conditions for electrolytic chlorination or bromination. The substances investigated have usually been readily oxidisable, and, as oxidation easily takes place at the same time as chlorination, most of the results have been unsatisfactory. Thus Zehrlant (*Zeitsch. Elektrochem.*, 1901, **7**, 501) found that if a solution of phenol containing potassium halides was electrolysed, oxidation took place without there being any substitution, but substitution occurred if the electrolyte consisted of concentrated hydrobromic acid and phenol. Similarly, Gilchrist (*J. Physical Chem.*, 1904, **8**, 539), on electrolysing solutions of aniline hydrochloride and hydrobromide, obtained only aniline-black, whilst in the presence of a large quantity of hydrobromic acid, tribromoaniline was formed. On the other hand, a process for the preparation of iodoform by electrolysis has been perfected and is used commercially.

Such electrolytic processes are easily regulated, and the amount of substitution depends on the current density and on the potential. The corresponding phenomena for reduction have been very fully investigated, and the exact conditions for the preparation of the various reduction products of nitrobenzene are now known.

In the electrolysis of a mixture of two salts, the two anions reach the anode at the same time, and therefore the conditions are favourable for the interaction of the discharged anions. If one of the salts is potassium chloride, the conditions favour the formation of a chlorination product of the other anion. This other anion must not be easily oxidised, and the acid from which it is derived must be readily soluble in water, for the solution tends to become acid at the anode and a

sparingly soluble acid would thus be precipitated. Potassium benzenesulphonate was found to satisfy all these conditions, and this paper gives an account of the earlier experiments which have been carried out with it.

The first experiments were made with a carbon anode, which was rapidly rotated in order to stir the solution. It was found, however, that the electrode was attacked, and a platinum electrode was substituted for it. This consisted of a piece of platinum foil 6 cm. \times 10 cm., bent into a cylinder, and, as this could not be conveniently rotated, a centrifugal glass stirrer was used. In order to protect the products of chlorination from possible reduction at the cathode, a porous pot was used. The solution of the sulphonate and of the chloride or bromide was placed inside the pot, and a solution of potassium halide was placed outside. The cathode was made from a piece of sheet iron. The current was obtained from a motor transformer capable of giving 15 amperes at 10 volts. When the circuit was first closed, the current was small, owing to the resistance of the pot, but it rapidly rose, and, after a few minutes, 4 amperes could be easily passed through the cell. After some time, however (half an hour), the resistance of the cell greatly increased, and only about 1 ampere could be passed even with 10 volts. This great increase in the resistance has not yet been explained.

This large internal resistance caused considerable heating, and, when the solution consisted of potassium benzenesulphonate (1 mol.) and potassium chloride (4 mols.), it was found that as the solution became hot a yellow, crystalline substance separated. This was found on analysis to consist of a mixture of trichloro- and tetrachloro-*p*-benzoquinone.

As this result seemed to be the effect of the high temperature, the experiment was repeated, keeping the solution near its boiling point, and it was found that the yield of tetrachloro-*p*-benzoquinone was then much greater. On the other hand, very little was formed when the solution was kept cold.

The most satisfactory method of separating the sulphonate and chlorosulphonates from the unchanged chloride was to evaporate the filtrate, dry the crops of crystals which separated, and extract from them the organic salts with hot alcohol. The crystals obtained from this alcoholic solution were then recrystallised from water. In this way, several crops of crystals were obtained, which were quite free from chloride. When the electrolysis had been carried out at the boiling point, these crystals all contained considerable quantities of chlorine, the chlorine content being determined by heating with lime and sodium carbonate and estimating the chloride. The following are the details for one of these experiments: The solution in the porous pot consisted of potassium benzenesulphonate (10 grams) and potassium

chloride (20 grams) dissolved in 130 c.c. of water. Seven and a-half ampere-hours were passed through the solution at its boiling point, and the amount of tetrachloro-*p*-benzoquinone obtained was 0.28 gram; this corresponds with only about 6 per cent. of the total electricity passed. On separating the unchanged sulphonate and its substitution products from the free chloride, several crops of crystals were obtained, all of which appeared to be mixtures of chlorosulphonates. Thus successive crops gave the following analyses:

No.	1.	2.	3.	4.	5.	6.
K	13.7	12.4	14.4	—	—	17.5
Cl	17.8	20.9	24.6	26.4	26.9	30.2

$C_6H_4Cl \cdot SO_3K$ requires $K = 16.9$; $Cl = 15.4$.

$C_6H_3Cl_2 \cdot SO_3K$ „ $K = 14.7$; $Cl = 26.7$.

$C_6H_2Cl_3 \cdot SO_3K$ „ $K = 13.1$; $Cl = 35.5$ per cent.

It therefore appears that monochloro-, dichloro-, and possibly also trichloro-sulphonates are formed under these conditions, but the figures show that none of the crops were homogeneous. The products of the electrolysis depend also in some way on the character of the electrode, for when a platinum-iridium gauze electrode was substituted for the foil, very little tetrachloro-*p*-benzoquinone was formed, and the quantity of substitution product was too small to be properly investigated.

When potassium bromide was used instead of potassium chloride, a considerable quantity of tetrabromo-*p*-benzoquinone was formed under those conditions which favoured production of the corresponding chloro-derivative. Analysis and melting-point determinations showed again that this product was not pure. A large quantity of bromate was also formed, but no bromosulphonic acids could be isolated.

Electrolysis of a solution containing the sulphonate and potassium iodide gave a quantity of free iodine which seemed to be without effect on the organic salt.

In the hope that the porous pot might be dispensed with, and the electrolysis thus carried out with a lower voltage, a small quantity of potassium dichromate was added to the solution before electrolysis. Although this is sufficient to protect the substances from reduction at the cathode in the preparation of chlorates, it seemed to be quite useless in this case, for no tetrachloro-*p*-benzoquinone was formed and no substituted sulphonic acids could be isolated.

The authors intend to continue these experiments, and to determine the exact conditions under which substitution takes place. They also intend to investigate the chlorination of other anions.

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(LIV.—*The Conductivities of the α -Oximino-fatty Acids.*

By JOHN KENNETH HAROLD INGLIS and LOTTIE EMILY KNIGHT.

DETERMINATIONS of the conductivities of aqueous solutions of the lower α -oximino-fatty acids were published by Hantzsch and Miolati (*Zeitsch. physikal. Chem.*, 1892, 10, 1), and from them they calculated the dissociation constants in the ordinary way.

They found that α -oximinopropionic acid ($K = 0.051$) is a weaker acid than the first member of the series, oximinoacetic acid ($K = 0.099$), and weaker also than the next higher, α -oximinobutyric acid ($K = 0.083$), whilst α -oximino-*n*-valeric acid ($K = 0.068$) is again weaker than α -oximinobutyric acid. The influence of the size of the alkyl group is not then a simple one; and starting from the assumption that all these acids have the *syn*-configuration of the hydroxyl and carboxyl groups, namely, $\begin{smallmatrix} R \cdot C_1 \cdot CO_2H \\ | \\ N \cdot OH \end{smallmatrix}$, they conclude that

the position of the hydroxyl varies irregularly with the size of the alkyl group, so that, whilst it never passes into the *anti*-position, its actual distance from the carboxyl increases and decreases alternately as the series is ascended. The data given, however, seem hardly sufficient to justify the introduction of this idea, and it will be noticed that any abnormality in the value for α -oximinopropionic acid would reduce the results to a series of gradually diminishing dissociation constants. Hantzsch and Miolati decided that their α -oximinovaleric acid was not pure because they found that the constant decreased with increasing dilution. It seemed therefore desirable to prepare the acids of this series, as far as possible, by a general method, to obtain them pure, and to re-determine their dissociation constants.

Preparation of the Acids.

The method used was that described by Locquin and Bouveault (*Bull. Soc. chim.*, 1904, [iii], 31, 1055). The alkyl derivative of acetoacetic ester was dissolved in twice its weight of concentrated sulphuric acid, the temperature being kept below 0° , and a solution of "chamber crystals" (theoretical quantity + 10 per cent. excess) in twice its weight of sulphuric acid was slowly added, the temperature still being kept below 0° . The product was poured on to broken ice, and the α -oximino-ester separated as an oil or solid. In most cases, this was directly hydrolysed with 40 per cent. aqueous potassium hydroxide, and the acid extracted with ether after acidifying with hydrochloric acid. The acids were recrystallised several times from ether, or a

mixture of ether and light petroleum, or from absolute alcohol, and, in some cases, finally from water. The equivalents were in all cases determined by titration with baryta.

(1) *Oximinodiacetic Acid*.—This acid is usually prepared from glyoxylic acid, but for these experiments it was prepared by the method given above. The ester does not in this case separate as an oil or solid, but it can be extracted with ether. The acid is then obtained by hydrolysis and crystallised from water. The crystals, which begin to melt at about 70° , are silky needles which effloresce in the air. The low melting point is due to the presence of a molecule of water of crystallisation, and this is lost if the crystals are left standing for three days over sulphuric acid. They then melt at 140 – 141° . Two determinations of the equivalent of the acid dried in this way gave 89.3 and 89.1 (theory = 89.0). Analysis gave the following results:

C = 26.50. H = 3.37.

$C_2H_3O_3N$ requires C = 26.98; H = 3.53 per cent.

The aqueous solution is apparently quite stable. No difference in the titre of an $N/16$ solution was found after standing three days.

(2) *α -Oximinopropionic Acid*.—This was prepared by the general method, using methylacetoacetic ester. After several recrystallisations from ether, and finally from water, it melted and decomposed at 180° , and the equivalent was found to be 103.7 (theory = 103.0). A second quantity was prepared by the action of hydroxylamine on an alkaline solution of pyruvic acid. This formed similar crystals, melting and decomposing at 180 – 181° . A solution ($N/16$) in water, kept at the ordinary temperature for five days, remained unchanged.

(3) *α -Oximinobutyric Acid*.—This was prepared from ethylacetoacetic ester. When crystallised from water, it forms short needles, melting and decomposing at 154° . The equivalent was found to be 117.5 (theory = 117.0).

(4) *α -Oximinovaleeric Acid*.—This was prepared from *n*-propylacetoacetic ester. It is sparingly soluble in water, from which it crystallises well, but it is better to crystallise it from absolute alcohol. Its colourless crystals melted and decomposed at 140° . The equivalent was found to be 134.4 (theory = 131). When warmed with water it partly decomposes.

Conductivity Measurements.

The measurements of conductivity were made according to Ostwald's method at 25° . The water had a specific conductivity of 2.1×10^{-6} . In order to test the method, measurements were carried out with potassium chloride and with succinic acid, and the resulting figures at dilutions from $N/16$ to $N/1024$ agreed with those given by Ostwald.

The values of the molecular conductivities at infinite dilution were

also determined by Ostwald's method. A $N/32$ solution of sodium hydroxide (from metal) was prepared, and portions were exactly neutralised by means of the respective acids, phenolphthalein being used as indicator. The conductivities of these solutions were then determined, and also the conductivities of the solutions obtained from them by dilution. The dilution was carried out until the solution was $N/1024$. According to Ostwald, the difference between μ_{32} and μ_{1024} is always the same ($=10$) for a monobasic acid.

TABLE I.

Molecular Conductivities of the Sodium Salts at 25°.

V	=	32.	64.	128.	256.	512.	1024.
Oximinodiacetic	$\mu =$	75.6	79.5	82.0	85.3	88.5	92.0
α -Oximinopropionic ...	$\mu =$	72.0	75.5	78.5	81.3	84.5	89.0
α -Oximinobutyric	$\mu =$	69.6	73.2	75.3	78.3	81.5	85.0
α -Oximinovaleic	$\mu =$	68.7	72.5	74.5	77.5	80.0	84.5

When these measurements (table I) were carried out, it was found that the Ostwald rule was not obeyed, and that $\mu_{1024} - \mu_{32}$ was about 15, instead of 10. As the acids are not weak acids, this result cannot be due to hydrolysis. It may indicate that a second ionisation takes place, and that when the hydrogen atom of the carboxyl group has been replaced by sodium, the hydrogen atom of the oximino-group can be partly ionised. This ionisation (too small to be detected by titration) would increase with increasing dilution, and might explain the deviations observed.

In these circumstances, in order to obtain the value μ_{∞} , a slightly different method was employed. If this ionisation did not take place, $\mu_{\infty} - \mu_{32}$ would, according to Ostwald, be equal to 13. Hence, as the ionisation probably does not take place in a solution of the acid, we can obtain μ_{∞} for the acid from the equation:

$$(\mu_{\infty} \text{ for a id}) = (\mu_{32} \text{ for sodium salt}) + 13 - 51 + 347 \\ = (\mu_{32} \text{ for sodium salt}) + 309,$$

51 and 347 being the conductivities of the sodium and hydrogen ions at 25° (Ostwald-Luther, *Phys. Chem. Messungen*, 415). The values thus obtained are:

Oximinodiacetic	$\mu_{\infty} =$	381 (386)
α -Oximinopropionic	$\mu_{\infty} =$	381 (383)
α -Oximinobutyric	$\mu_{\infty} =$	379 (380)
α -Oximinovaleic	$\mu_{\infty} =$	378 (378).

The values in brackets are those obtained by calculation from the number of atoms in the molecule. Hantzsch and Nioleti used much lower values (356—365), the conductivity of the hydrogen ion being then given a much smaller value than at present.

TABLE II.

*Molecular Conductivities of the Acids.**Oximinodiacetic Acid.* $\mu_{\infty} = 384$.

$V =$	16.	32.	64.	128.	256.	512.	1024.
μ	46.1	63.2	85.9	114.0	148.4	188.2	225.8
K	0.102	0.101	0.101	0.098	0.095	0.092	0.095

Mean value $K = 0.096$. *α -Oximinopropionic Acid.* $\mu_{\infty} = 381$.

(1) From methylacetacetic ester:

$V =$	16.	32.	64.	128.	256.	512.	1024.
μ	32.1	44.6	61.5	82.7	110.4	144.2	185.4
K	0.048	0.049	0.049	0.047	0.046	0.045	0.045

Mean value $K = 0.047$.

(2) From pyruvic acid:

$V =$	16.	32.	64.	128.	256.	512.	1024.
μ	32.3	45.0	61.9	84.1	111.3	146.0	184.7
K	0.049	0.049	0.049	0.049	0.047	0.047	0.045

Mean value $K = 0.048$. *α -Oximinobutyric Acid.* $\mu_{\infty} = 379$.

(a) $V =$	16.	32.	64.	128.	256.	512.	1024.
μ	40.5	55.3	74.8	99.2	128.4	156.0	199.8
K	0.080	0.078	0.076	0.072	0.068	0.056	0.053

Mean value $K = 0.070$.

(b) $V =$	16.	32.	64.	128.	256.	512.	1024.
μ	40.4	54.6	73.3	96.1	125.0	155.9	199.4
K	0.080	0.076	0.072	0.067	0.063	0.059	0.057

Mean value $K = 0.068$.

H. and M. (recalc.):

	0.077	0.077	0.075	0.070	0.063	0.056	0.053
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 α -Oximinovaleic Acid. $\mu_{\infty} = 378$.

$V =$	16.	32.	64.	128.	256.	512.	1024.
μ	36.5	49.4	64.9	83.9	107.1	133.5	162.1
K	0.064	0.061	0.056	0.050	0.044	0.038	0.031

From first three, mean value $K = 0.060$.

H. and M. (recalc.):

K	—	0.060	0.059	0.058	0.057	0.054	0.050
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In the case of the last two acids, a freshly-made solution showed an increase of conductivity with time for about two hours before the

falling off, due to decomposition, became noticeable. Thus an approximately $N/16$ solution of α -oximinobutyric acid had a molecular conductivity of 37.0 immediately after making up, but, after one and a-half hours, the value had risen to 41.4. In the case of the lower acids, no such increase was observed. The change, however, was not very rapid, and the values of the conductivities given in the tables are those obtained as soon as the temperature had become constant. Exact measurements in regard to the change have yet to be made.

Discussion of Results.

The conductivity measurements given above agree on the whole with those of Hantzsch and Miolati, but give in the first two cases slightly higher values for the dissociation constants. It appears that the rate of decomposition of the oximino-butyric and -valeric acids has been much greater than in their measurements, although both sets of figures show the same distinct falling off of the constant. From their results, Hantzsch and Miolati drew the conclusion that the acids exist in only one form, and, by comparison with other cases in which two forms are known (for example, oximinophenylacetic acid), this form appeared to be the *syn*-form, the *anti*-form being usually a much stronger acid. The anomalous values of the conductivity constants were supposed to be due to variations in the distance of the hydroxyl of the oximino-group from the carboxyl group. In the case of oximinopropionic acid, this hydroxyl was supposed to be nearer the carboxyl group than in the other acids, and thus to have a weakening effect on the strength of the acid. It is difficult to see how this can be the case. The measurements of the conductivities of the sodium salts point to the oximino-group being itself partly ionised, and it would certainly be acting as an acid group in that ionisation. Therefore, comparing this case with that of maleic and fumaric acids, the *syn*-position should correspond with the stronger and unstable acid, and a high value of the dissociation constant would therefore be coupled with instability of the acid itself. Now, if we compare the acids with one another, we find that oximinopropionic acid has the highest melting point, and this is also the case with its ester (table III).

TABLE III.

Melting Points of the Acids and Esters.

	Acid.	Ethyl ester.	K.
Oximinobacetic	140°	oil	0.046
α -Oximinopropionic	180	68–69°	0.047
α -Oximinobutyric	154	58	0.069
α -Oximinovaleric	140–144	48	0.050
α -Oximinoisovaleric	150	56	—
α -Oximinoisobutylic	150–151	60	—

The melting point is, however, not a true melting point, for decomposition takes place with formation of water, carbon dioxide, and a nitrile. Consequently, the apparent melting point is really *only the temperature at which this decomposition takes place*. As it takes place at a higher temperature with oximinopropionic acid, the probability is that the carboxyl and hydroxyl groups are further apart in that acid than in the others, and not nearer together, as Hantzsch and Miolati supposed. This view is supported by the fact that aqueous solutions of the two lower acids are stable, even on heating, whilst the two higher acids decompose even in solution at the ordinary temperature. Thus, in six days, at the ordinary temperature, an aqueous solution of oximinobutyric acid decreased in strength from 0.0625*N* to 0.0317*N*, and a solution of oximinovaleic acid decreased from 0.062*N* to 0.049*N* in two days and to 0.027*N* in six days. This behaviour is what one would expect on examining the structures of the molecules. The methyl group in oximinobutyric acid is in the 1:5-position with respect to the hydroxyl of the oximino-group, and in oximinovaleic acid it is in the 1:6-position. This structure would therefore, according to Bischoff, tend to force the hydroxyl nearer the carboxyl group, and the substance would be less stable. This initial rise of conductivity in these acids indicates that two distinct forms of the acid exist, and that the one is slowly formed from the other in solution. It appears therefore that the relations between the conductivities and configurations are not so simple as was supposed, and, with our present knowledge of these substances, no definite conclusion can be drawn. It is therefore intended to continue these experiments, and to examine the conductivities and stabilities of the higher acids of the series.

In conclusion, the authors are glad to take this opportunity of expressing their thanks to Dr. A. W. Stewart for his help during the course of the investigation.

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CLX.—*The Formation of Ethers from Compounds of the Benzoïn Type.*

By JAMES COLQUHOUN IRVINE, Ph.D., D.Sc., and DAVID McNICOLL, M.A., B.Sc. (Carnegie Scholar).

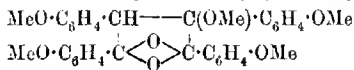
It has been shown in a former communication (Trans., 1908, 93, 950) that the action of hydrogen chloride and methyl alcohol on ordinary benzoïn is not a simple one, and results in the production, in addition to benzoïn methyl ether, of alkylated furan derivatives. We have extended our work in order to ascertain if the formation of such by-products is general, and the present paper describes the results obtained by applying Fischer's method of alkylation (*Ber.*, 1893, 26, 2412) to various compounds possessing the benzoïn structure.

We find that the action of hydrogen chloride on an ethyl-alcoholic solution of benzoïn gives results widely different from those previously observed with solutions in methyl alcohol. No complex condensation compounds are formed, and benzoïn ethyl ether (m. p. 62–63°) constitutes the main product. Some ambiguity seems to exist with regard to the latter compound, as Jena and Limpricht (*Annalen*, 1870, 155, 97) describe it as a product of the interaction of benzoïn, ethyl alcohol, and sodium ethoxide, melting at 95°. This value, although it does not agree with that (62°) subsequently found by Fischer, who used the hydrochloric acid method, or by Lander (Trans., 1900, 77, 733), who afterwards obtained the compound by the silver oxide reaction, has nevertheless retained its place in the literature. In order to settle this point, we have repeated both Fischer's and Lander's preparations, and find their products to be identical and to contain one ethoxyl group, as shown by the results of Zeisel determinations. The correct melting point of benzoïn ethyl ether is therefore 62–63°. As it appeared possible that the compound described by Jena and Limpricht might be isomeric with benzoïn ethyl ether, and thus be an alkylated furan derivative, we have also repeated their experiments. We find that their observations are so far correct, in that a substance, apparently homogeneous and melting constantly at 93–95° after several crystallisations from alcohol, was obtained as a product of their reaction. By a curious coincidence, the crystalline form, solubilities, and analytical composition of the substance agreed approximately with those of benzoïn ethyl ether, but Zeisel determinations gave entirely negative results. After fusion and recrystallisation from dry ether, the substance was ultimately separated into hydrobenzoïn and isohydrobenzoïn.

It would thus appear that Jena and Limpricht's "ethyl benzoïn" is either the hydrated form of *isohydrobenzoïn* (m. p. 95—96°) described by Forste and Zincke (*Annalen*, 1876, 182, 279) or the mixture of isomeric hydrobenzoïns, which melts constantly at 95° (*Annalen*, 1879, 198, 152). The agreement of the analytical figures with those required for benzoïn ethyl ether must thus be regarded as a coincidence, the high carbon content being due to the presence of impurities. The observations recorded by Jena and Limpricht, that the so-called "ethyl benzoïn" was unaltered by sodium amalgam, but was oxidised by nitric acid to give benzoïn and benzil, are in agreement with either of the above explanations as to the nature of the substance.

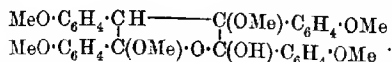
In the case of anisoin, we find that Fischer's process does not yield any appreciable quantity of anisoin methyl ether, but results in partial oxidation to anisil, and in the formation of two substituted furan derivatives analogous to those previously obtained from ordinary benzoïn. Although the process was modified in various ways by altering the concentration of acid and the temperature at which the reaction was carried out, the result was invariably the same, and normal methylation did not take place.

The condensation compound first produced melted at 218—219°, and analyses agreed with the formula $C_{33}H_{22}O_7$, containing five methoxyl groups. As is frequently the case with anisoin derivatives, the substance was easily resinified, and thus few reactions could be studied to elucidate its constitution. Its ready oxidation to anisil, however, and conversion by Baeyer's process into a mixture of *p*-dimethoxystilbene and deoxyanisoin, show that the compound is comparable with $\alpha\beta$ -dibenzoyl- α -methoxydibenzyl, which is obtained from benzoïn in a similar reaction. We therefore regard the substance as a 4 : 4' : 4'' : 4'''-pentamethoxy- $\alpha\beta$ -dibenzoyldibenzyl,



The second product of the condensation melted at 264—265°, and was formed in greater quantity towards the end of the reaction, presumably by the addition of methyl alcohol to the compound of lower melting point just referred to. The analytical composition was the same as that required for anisoin methyl ether, but the molecular weight was twice as great, pointing to the formula $C_{34}H_{30}O_8$. The compound was further distinguished from anisoin methyl ether by its sparing solubility and high melting point, and was analogous in every respect to 2-hydroxy-3 : 5-dimethoxytetraphenyltetrahydrofuran, which is produced under similar conditions from benzoïn. The compound is

therefore regarded as 2-hydroxy-3:5-dimethoxytetra-anisyltetrahydrofuran:



The action of hydrogen chloride on an ethyl-alcoholic solution of anisoin gave, on the other hand, no complex condensation products, the reaction yielding a small quantity of anisoin ethyl ether contaminated, however, with anisil, from which it could not be completely separated by crystallisation. Similar experiments were made with *o*-dimethoxybenzoin, which, when dissolved in methyl alcohol and subjected to the action of hydrogen chloride, only deposited extremely minute quantities of crystalline matter, the amount of which did not admit of further examination. Normal methylation, however, proceeded to some extent with the formation of small quantities of *o*-dimethoxybenzoin methyl ether, but the process was only successful when the solution contained about 15 per cent. of hydrogen chloride. In the case of less strongly acid solutions, the benzoin was recovered unaltered, whilst at higher concentrations *o*-methoxybenzoic acid was, owing to molecular rupture, formed in quantity.

On applying the same process to furoin, we found that even small quantities of hydrogen chloride acted on a methyl-alcoholic solution of the compound, giving a highly-coloured liquid from which a dark green, crystalline precipitate separated. The product was practically insoluble in ordinary solvents, but, without further purification, gave analytical figures agreeing with those required for furoin methyl ether. For the sake of comparison, we prepared the latter substance from furoin by the silver oxide method, and obtained it in the form of a readily soluble syrup, so that the insoluble compound referred to above is not the product of normal methylation, but is doubtless analogous to the substance, melting at 285°, previously obtained in a similar reaction from benzoin. According to this view of its structure, the compound possesses a unique constitution, five furan residues being directly linked. The substitution of ethyl for methyl alcohol in the above reaction led to no definite result, the furoin either being recovered unaltered or undergoing oxidation.

It will thus be seen that the hydrochloric acid method of alkylation does not give very uniform results when applied to benzoin. When methyl alcohol is used as the solvent, furan derivatives are formed, and, as a rule, the alkyl ethers formed are contaminated with oxidation products, which render purification difficult. On the other hand, the silver oxide reaction gives extremely good yields of the desired compounds, which crystallise readily. The methyl ethers of benzoin, anisoin, *o*-dimethoxybenzoin, and furoin are thus produced in almost

quantitative amount, and the yields of the corresponding ethyl ethers are also satisfactory.

The following table summarises the results obtained by applying the two alternative methods of alkylation to the various benzoinz studied. The numbers express the percentage yields of the different products in terms of the weight of benzoin used:

	Methyl alcohol and hydrogen chloride.	Methyl iodide and silver oxide.	Ethyl alcohol and hydrogen chloride.	Ethyl iodide and silver oxide.
Benzoin	50—75% Methyl ether. 20—35% Furan derivatives. Benzil also formed.	Quantitative methylation. (A)	70% Ethyl ether. No furan derivatives.	70% Ethyl ether. No furan derivatives.
Anisoin	No methylation. 41% Furan derivatives. 42% Anisil.	Quantitative methylation. (B)	25% Ethyl ether. Anisil also formed.	Quantitative ethylation.
<i>o</i> -Dimeth- oxybenzoin	Very little methylation. <i>o</i> -Methoxybenz- oic acid formed.	Quantitative methylation. (C)	—	—
Furoin	No methylation. 10% Furan derivatives.	80% Methyl ether.	No ethylation. Oxidation products formed.	Very little action.

(A) Trans., 1907, **91**, 1391. (B) Trans., 1907, **91**, 543. (C) Trans., 1901, **79**, 672.

EXPERIMENTAL.

Action of Ethyl Alcohol and Hydrogen Chloride on Benzoin.

This reaction, already carried out by Fischer, was repeated for reasons given in the introduction. Twelve grams of benzoin were dissolved in 700 grams of absolute ethyl alcohol, and dry hydrogen chloride was passed through the solution. In different experiments, the saturation with the gas was carried out at 60° and 10° respectively, a greater proportion of solvent alcohol being of course necessary in the second instance. In each case the result was the same; the liquid remained quite clear even after standing for some days, and, when poured into water, gave a copious, white precipitate. The crystalline product, after spreading on porous porcelain and recrystallisation from light petroleum, melted at 62—63°. Analysis showed the compound to have the composition of benzoin ethyl ether, and a Zeisel determination confirmed the presence of one ethoxyl group:

Found: OEt = 19.64.

$C_{14}H_{11}O(OEt)$ requires OEt = 18.75 per cent.

Action of Ethyl Alcohol and Sodium Ethoxide on Benzoïn.

The directions given by Jena and Limpricht (*loc. cit.*) for this reaction were adhered to, and the same weights of the reacting substances were used. The solid product, when fractionally crystallised from absolute alcohol, gave a series of crystalline crops, the indefinite melting points of which showed that little separation of the constituent substances had taken place. The use of dilute alcohol as a crystallising medium led to more satisfactory results. The less soluble compound was shown to be hydrobenzoïn, and from the mother liquors a product crystallising in prisms and melting at $93-95^{\circ}$ was obtained, as described by Jena and Limpricht.

Recrystallisation from alcohol did not affect the melting point, and, as an analysis gave figures agreeing approximately with those quoted by the latter observers, the substance apparently possessed the composition of benzoïn ethyl ether, but a Zeisel determination gave a negative result:

Found: C = 80.60; H = 6.89; OEt = Nil.

$C_{14}H_{11}O(OEt)$ requires C = 80.00; H = 6.66; OEt = 18.75 per cent.

Jena and Limpricht found:

C = 80.30; H = 6.70 per cent.

The properties of the substance agreed closely with the hydrated form of isohydrobenzoïn, but the carbon value found is too high. This, however, may have been due to the presence of traces of the compound $C_{26}H_{26}O_2$, the carbon content of which is considerably higher. On heating at 105° for four hours, the fused mass became semi-solid, and, when then recrystallised from ether, gave two products melting at $118-120^{\circ}$ and $128-130^{\circ}$, which analyses showed to be isohydrobenzoïn and hydrobenzoïn respectively.

It may be mentioned here that no ethyl ethers of any kind are formed in the above reaction. In an experiment duplicate in every way with that described by Jena and Limpricht, the total solid product was crystallised in eight separate fractions, each of which was examined by Zeisel's method. In every case a negative result was obtained.

Condensation of Anisoin with Methyl Alcohol.

The anisoin used was obtained from Kahlbaum, and melted at $110-111^{\circ}$. On passing dry hydrogen chloride into a well-cooled solution containing 35 grams of the compound in 1200 c.c. of anhydrous methyl alcohol, the liquid rapidly acquired a brilliant red colour, which did not appreciably darken during the further solution of the gas. When the concentration of the acid amounted to 5 per cent., a sparingly

soluble precipitate commenced to form, which was filtered at intervals. After the liquid had remained at the temperature of the room for twelve hours, no further solid product was obtained on saturating the filtrate with hydrogen chloride, and identical results were obtained in similar experiments in which the concentration of the acid amounted to 10, 20, and 30 per cent. The crystalline precipitate referred to above weighed 14.5 grams, and, after washing with methyl alcohol until free from acid, was extracted several times with a large excess of boiling acetone. The undissolved residue (4 grams) consisted of minute, irregular plates, which, without further purification, melted sharply at 264—265°, whilst the acetone extract deposited on concentration a substance crystallising in rhomboidal plates, which, after recrystallisation from the same solvent, melted at 218—219°.

Examination of the strongly acid mother liquors obtained in each of the above preparations showed that in no case had methylation of the anisoin taken place. The bright red solutions when poured into water gave a semi-crystalline oil, which solidified on standing. After washing with water and two recrystallisations from ethyl alcohol, this product was obtained in the characteristic form of anisil (m. p. 133°), the yield of which amounted to 42 per cent. of the weight of anisoin used. The united mother liquors collected during the purification of the anisil contained a little resinous matter, and no anisoin methyl ether could be detected.

Examination of the Compound melting at 218—219°.—The compound is insoluble in water, sparingly soluble in ether, acetone, or alcohol, but is readily dissolved by benzene or chloroform. Analysis gave:

C = 73.26; H = 6.20; OMe = 29.47.

$C_{28}H_{12}O_2(OMe)_5$ requires C = 73.33; H = 5.93; OMe = 28.70 per cent.

The substance, which was without action on Fehling's solution, even after boiling with hydrochloric acid, was readily oxidised to anisil when warmed in acetic acid solution with nitric acid. When boiled with acetic anhydride and sodium acetate, it was recovered unaltered, and it also resisted the action of acetic anhydride containing sulphuric acid so long as the solution was kept cold. When gently warmed, however, complete decomposition took place.

The action of hydrogen iodide on the compound was also investigated, but, as is frequently the case with anisoin derivatives, the product was an uncrystallisable resin. When mixed with zinc dust and distilled in a current of carbon dioxide, a crystalline distillate was obtained, from which by purification from alcohol two products were separated. The more sparingly soluble substance crystallised in glistening leaflets melting at 209—211°, readily recognisable as *p*-dimethoxystilbene, which has already been isolated (Trans., 1907, 91, 542) as a reduction

product of anisoin derivatives. The more soluble compound was identified as deoxyanisoin by the melting point and conversion into the corresponding oximo.

Examination of the Compound melting at 263–265°.—This substance, which is isomeric with anisoin methyl ether, resembles the compound of lower melting point, but is much less soluble in organic solvents generally:

Found: C = 71.34; H = 6.58; OMe = 31.86.

$C_{23}H_{18}O_2(OMe)_6$ requires C = 71.33; H = 6.30; OMe = 32.52 per cent.

The molecular weight, determined in chloroform solution by the boiling point method, agreed with the formula $C_{23}H_{18}O_8$ (Found 551; theory requires 572). The reactions of the compound were very similar to those already described for the substance of lower melting point. Thus it was unacted on by boiling with acetic anhydride and sodium acetate, was easily resinified by the action of hydrogen iodide, and underwent ready oxidation to anisil when boiled with alkaline potassium permanganate solution. On adding the compound to acetic anhydride containing a little concentrated sulphuric acid, a brilliant violet solution was obtained, which gradually passed through a series of colour changes, finally becoming red. On pouring into water, however, the bulk of the original material was recovered unaltered, and, in addition, a small quantity of resinous matter was isolated.

Action of Ethyl Alcohol and Hydrogen Chloride on Anisoin.

Three grams of anisoin were dissolved in 120 c.c. of absolute ethyl alcohol, and dry hydrogen chloride was passed into the well-cooled solution until the concentration of the acid amounted to 25 per cent. Even after preserving the solution for several days, no sparingly soluble products were obtained. The liquid was accordingly examined to ascertain if normal ethylation had occurred. When poured into water, a crystalline precipitate was formed, which, after filtration and washing with water, was recrystallised from alcohol. The bulk of the product consisted of anisoin ethyl ether, mixed, however, with anisil, which could not be completely separated by any process of crystallisation.

Action of Methyl Alcohol and Hydrogen Chloride on o-Dimethoxybenzoin.

o-Methoxybenzaldehyde was prepared from salicylaldehyde according to the method previously described by one of us (Irvine, Trans., 1901, 79, 668). The yield of alkylated aldehyde was satisfactory, 117 grams of constant boiling product being obtained from 120 grams of salicylaldehyde, but the compound did not crystallise readily, even

when repeatedly distilled. This may be due to the fact that "käufliches" salicylaldehyde was used, and, although we were unable to detect any noticeable impurities either in the starting material or in the methoxybenzaldehyde prepared from it, the subsequent condensation to the benzoin gave very unsatisfactory yields. The substitution of Voswinkel's method of preparing the etheric aldehyde did not result in any improvement, the yield of *o*-dimethoxybenzoin only amounting to about 20 per cent. of the theoretical amount. The large quantities of oily by-products formed during the condensation seemed to consist largely of nitriles.

The treatment of the benzoin with methyl alcohol and hydrogen chloride was carried out in the usual way, and, as explained in the introduction, when the concentration of the acid amounted to 5 per cent., the benzoin was recovered unaltered. Using a 15 per cent. solution of hydrogen chloride, the liquid became bright yellow, and deposited a minute quantity of crystalline matter, which, as it melted between 150° and 160°, did not consist of any known derivative of the benzoin. On pouring the filtrate into water, a crystalline precipitate was obtained, which, after several recrystallisations from ether, melted at 59—60°, and therefore consisted of *o*-dimethoxybenzoin methyl ether; only a small amount of it, however, was obtained. Using higher concentrations of hydrogen chloride (30 to 60 per cent.), the solution became bright red, no sparingly soluble by-products were formed, and, when diluted with water, a semi-crystalline oil was precipitated. After spreading on a tile and recrystallising from a mixture of alcohol and light petroleum, the acid product melted at 97—98°. Analyses showed the compound to be *o*-methoxybenzoic acid.

Action of Methyl Alcohol and Hydrogen Chloride on Furoin.

The details of the process were the same as already described for other benzoin. The liquid rapidly darkened during solution of the gas, and was quite black when the concentration of the acid amounted to 10 per cent. On standing overnight, a dark sooty deposit formed on the walls of the flask, which appeared to be carbonaceous matter. When filtered and washed with alcohol, however, it was apparent that the product possessed a dark olive-green colour, and was definitely crystalline. A similar result was obtained with solutions containing 2.5 per cent. of hydrogen chloride, and by leaving furoin in contact with methyl alcohol containing 5 per cent. of the acid. In the latter case, the furoin passed gradually into solution, and the dark-coloured precipitate afterwards separated. The yield was about 10 per cent. of the furoin used.

No definite melting point could be obtained for the compound, which

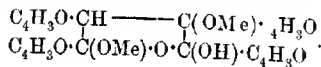
began to fuse with decomposition at about 200° . It was quite insoluble in water and in the common organic solvents with the exception of benzene, in which it dissolved to a slight extent, giving highly-coloured solutions. It was thus impossible either to determine the molecular weight or to recrystallise the substance, which was not further purified. Judging from previous experience in similar reactions, the product is doubtless a mixture of the two complex furan derivatives $C_{21}H_{16}O_7$ and $C_{22}H_{26}O_8$. Analysis supported this view:

Found: C = 64.63; H = 5.17.

$C_{21}H_{16}O_7$ requires C = 66.31. H = 4.21 per cent.

$C_{22}H_{26}O_8$ " C = 64.08. H = 4.85 " "

A Zeisel determination gave OMe = 14.32, from which we conclude that the specimen was essentially $C_{26}H_{14}O_6(OMe)_2$ (theory requires OMe = 15.05 per cent.). On the analogy of our results obtained with other benzoin, we believe the compound to be 2-hydroxy-3:5-dimethoxy-tetra- α -furyltetrahydrofuran:



Ethylation of Benzoïn by the Silver Oxide Method.

Lander (*loc. cit.*) has already prepared benzoïn ethyl ether by the silver oxide method, but found that the reaction resulted in partial molecular rupture, benzaldehyde and ethyl benzoate being obtained in addition to benzoïn ethyl ether, the yield of which amounted to 40 per cent. of the weight of benzoïn used. In repeating his preparation with a view to comparing his product with Fischer's, we have succeeded in eliminating these secondary reactions to a considerable extent, the preparation being more successful if the boiling point of the solution is lowered by the addition of ether. The reaction was carried out with benzoïn (1 mol.), silver oxide (3 mols.), and ethyl oxide (9 mols.), sufficient dry ether being added to reduce the boiling point of the solution to 50° . During heating at $48-50^{\circ}$ for three hours, the benzoïn passed gradually into solution, the temperature hereafter being maintained at $55-60^{\circ}$ for eight hours. On extracting with boiling ether and evaporation of the solvent, a colourless oil was obtained which solidified completely and consisted of benzoïn ethyl ether; this, after recrystallisation from light petroleum, melted sharply at $62-63^{\circ}$. The yield amounted to more than 70 per cent. of the weight of benzoïn used.

Ethylation of Anisoin by the Silver Oxide Method.

The reaction was carried out as usual, the anisoin (1 mol.) being dissolved in ethyl iodide (6 mols.) to which a little acetone had been added, and the solution boiled for several hours with silver oxide (3 mols.). The product was extracted with boiling ether, and crystallised very readily on concentration of the solvent. The compound, when purified by recrystallisation from 50 per cent. alcohol, melted at 103—104°. The yield was quantitative:

Found: C=71.81; H=6.93.

$C_{13}H_{20}O_4$ requires C=72.00; H=6.70 per cent.

0.1663 gave, by Zeisel's method, 0.3850 AgI. OMe=20.38;
OEt=14.83.

$C_{14}H_{18}O(OMe)_2 \cdot OEt$ requires OMe=20.66; OEt=15.00 per cent.

The compound possessed the usual properties of such substances, but the melting point is somewhat irregular, being much higher than that found for the corresponding ether of ordinary benzoin.

Methylation of Furoin by the Silver Oxide Method.

This reaction presented some difficulty on account of the sparing solubility of furoin in methyl iodide and its ready oxidation to furil. When silver oxide was added to a solution of the benzoin in a mixture of methyl iodide and acetone, the reaction was very vigorous, a number of striking colour changes took place, and the product obtained was a bright red syrup of a complex nature. The use of methyl alcohol to facilitate the solution of the furoin in methyl iodide apparently led to less extensive decomposition, but the main product was found to be furil. Ethyl acetate proved to be a more satisfactory solvent, but the boiling point of the solution was too high and oxidation ensued. The process was finally carried out by adding silver oxide (2 mols.) to a solution of furoin (1 mol.) in ethyl acetate containing methyl iodide (5 mols.), sufficient dry ether being added to reduce the boiling point of the solution to 50°. The mixture was boiled for six hours and worked up as usual. The product, after two alkylations, was a clear, yellow, neutral syrup, readily soluble in organic solvents, which decomposed on heating to 80°.

The analysis which was therefore carried out without further purification gave results agreeing approximately with those required for furoin methyl ether. No crystalline derivative could be obtained. The ethylation of furoin by the silver oxide method was also

attempted under similar conditions, but in each experiment the bulk of the benzoin was recovered unaltered.

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CLVI.—*Studies of the Perhalogen Salts. Part II.*

By CHARLES KENNETH TINKLER.

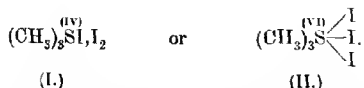
SOME preliminary results of an investigation on the formation of the iodine additive compounds of iodides, bromides, and chlorides as shown by means of ultra-violet absorption spectra were given in a former paper (Trans., 1907, 91, 997). It was found that, whilst dilute aqueous solutions of iodine, an iodide, a bromide, or a chloride have no characteristic ultra-violet absorption spectra, the periodides containing the groups I_3 , BrI_2 , and ClI_2 give rise to three distinct types of absorption spectra, each showing well-defined absorption bands.

In that paper it was pointed out that the method of investigation might be applied not only for the detection of the presence of a periodide in a given solution, but also for its quantitative estimation.

In the present paper an account is given of the study of other iodine additive compounds, and also of some experiments on the formation of perbromides.

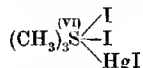
The Periodides of Alkylsulphine Salts.

In 1885 a series of perhalogen salts derived from the alkylsulphine salts was described by Dobbin and Masson (Trans., 1885, 47, 56), who pointed out that these substances might be represented by formulæ such as



In the one case the sulphur atom is quadrivalent, and in the other, sexavalent. Dobbin and Masson favour formula (II) for these sub-

stances. Hilditch and Smiles have recently (Trans., 1907, 91, 1396) adduced evidence in favour of the formula



for the mercuric iodide additive compounds of alkylsulphine iodides, and this view, as they point out, is strongly supported by the results obtained by Pope and Neville (Trans., 1902, 81, 1037), who found that the mercuric iodides of the trialkylsulphine iodides are incapable of resolution. It might therefore be assumed that the corresponding iodine additive compounds would be represented by formula (II).

Since it has been found that the group I_3 possesses such highly characteristic absorption spectra, it was thought that an investigation of the ultra-violet absorption spectra of these iodine additive compounds might throw some light on their constitution, as only a substance of formula (I) would possess the characteristic absorption of the I_3 group.

On the addition of trimethylsulphine iodide to an aqueous solution of iodine, the ultra-violet absorption spectra which are obtained are identical with those of a solution of iodine containing potassium iodide. Similarly, aqueous solutions of iodine to which trimethylsulphine bromide or chloride has been added, give spectra identical with those of solutions of iodine containing potassium bromide and chloride respectively.

It would appear, therefore, that in aqueous solution the substances have the formulæ $(\text{CH}_3)_3\text{S}^{(\text{VI})}\text{I}_2$, $(\text{CH}_3)_3\text{S}^{(\text{VI})}\text{BrI}_2$, and $(\text{CH}_3)_3\text{S}^{(\text{VI})}\text{ClI}_2$, and are true perhalogen salts.

The actual configuration of the groups of the three halogen atoms will be discussed later. On the addition of trimethylsulphine iodide to a chloroform solution of iodine, the spectra obtained are identical with those of an aqueous solution of iodine containing this or other soluble iodide. The compound therefore appears to have the structure (I) in chloroform solution also.

A specimen of the mercuric iodide compound of trimethylsulphine iodide was prepared according to Hilditch and Smiles's method (*loc. cit.*), and its absorption spectra examined. The substance showed no indication of the absorption bands characteristic of the I_3 group. This result would be expected, as this substance is certainly not a periodide.

Quinoline Tri-iodide.

It appeared of interest, for purposes of comparison, to examine the absorption spectra of a periodide of a cyclic base, and for this purpose quinoline tri-iodide was selected.

The absorption bands due to the I_3 group are observed in such dilute solution that the presence of the quinoline nucleus should be practically without effect on the spectra.

Quinoline tri-iodide was prepared by the addition of a solution of iodine in potassium iodide to a solution of quinoline sulphate (Dafert, *Monatsh.*, 1883, 4, 509). The spectra of solutions of this substance in chloroform and alcohol are practically identical with those of a solution of iodine containing excess of potassium iodide. The substance therefore appears to contain the true periodide group, as is expected from the ordinary reactions of the substance.

Some experiments were carried out to determine the amount of periodide produced by the addition of successively large quantities of substituted ammonium iodides to a chloroform solution of iodine. It was found that in this case the amount of periodide produced is almost directly proportional to the amount of iodide added, whereas in the case of an aqueous solution of iodine this is not the case.

Thus the spectrum of a layer 25 mm. thick of an $N/1000$ solution of iodine in chloroform, containing sufficient tetrapropylammonium iodide to combine with one twenty-fifth of the iodine in the solution, is the same as that of a layer 5 mm. thick of a solution containing five times that amount of iodide. The same spectrum is also given by a layer 1 mm. thick of a solution containing twenty-five times the amount of iodide contained in the first solution, that is, sufficient iodide to combine with the whole of the iodine. Similar results were obtained with tetraethylammonium iodide.

Abegg and Hamburger (*Zeitsch. anorg. Chem.*, 1906, 50, 403) have studied the stability of the higher polyiodides of the alkali metals in the solid state by estimating the amount of iodine withdrawn from a benzene solution of this substance by shaking with various iodides. It was found that the stability in the case of the higher polyiodides of the alkali metals was increased with increasing atomic weight of the metal.

From an examination of the spectra of solutions of iodine which contain equivalent small quantities of the iodides of these metals and of ammonium iodide, it does not appear possible, from the experiments already undertaken, to detect any difference in the stability of the tri-iodides of these metals, as the spectra produced are in all cases the same.

By the addition of equivalent quantities of tetra-methyl-, -ethyl-, and -propyl-ammonium iodides to an aqueous alcoholic solution of iodine, exactly the same spectra are obtained. It would appear from this result that the tri-iodides of these substances in aqueous alcoholic solution are equally stable.

Some preliminary experiments on the effect of temperature on the stability of the periodides have been carried out. A layer 65 mm. thick of an $N/4000$ solution of iodine in water containing 0.01 per cent. of potassium iodide was photographed, and the solution was then warmed to 30° . From the spectra of the solution at 30° , it is seen that some of the periodide is decomposed, as the absorption bands due to the I_3 ions tend to disappear. (A slightly greater thickness of layer at 30° was photographed to allow for expansion.) On cooling, the bands gradually reappear, showing that the periodide is reproduced. The spectra, however, still show a slight difference from those of the original solution, owing to the partial loss of iodine.

Exactly similar results are obtained by heating a solution of iodine containing a bromide or a chloride. The bands due to the BrI_2 and ClI_2 ions tend to disappear at the higher temperature.

It is hoped to carry out further experiments in this connexion.

Perbromides.

The formation of additive compounds of bromine and potassium bromide has been investigated by Wildermann (*Zeitsch. physikal. Chem.*, 1893, **11**, 407) and Roloff (*Zeitsch. physikal. Chem.*, 1894, **13**, 327). Worley (*Trans.*, 1905, **87**, 1107) found that a solution of bromine in potassium bromide at low concentrations contained only the tribromide, KBr_3 . Berthelot (*Compt. rend.*, 1885, **100**, 761) found from the heat of solution of bromine in hydrochloric acid that a substance HCl, Br_2 was produced.

As mentioned in the former paper on perhalogen salts, it was found that on the addition of potassium bromide to bromine water the spectra of the solution show a well-defined absorption band, whereas neither bromine nor potassium bromide at that particular concentration shows any absorption in the ultra-violet.* It seemed possible therefore that the formation of perbromides might also be investigated by this method.

Exactly the same spectra were obtained by adding to the aqueous solution of bromine the bromides of the following metals: sodium, potassium, rubidium, calcium, strontium, barium, magnesium, and cadmium, and also by employing hydrobromic acid, ammonium, tetramethyl- and tetraethyl-ammonium bromides (Fig. 1). All these solutions therefore contain the group Br_3 , and it is to the presence of this group that the absorption band in each case is due.

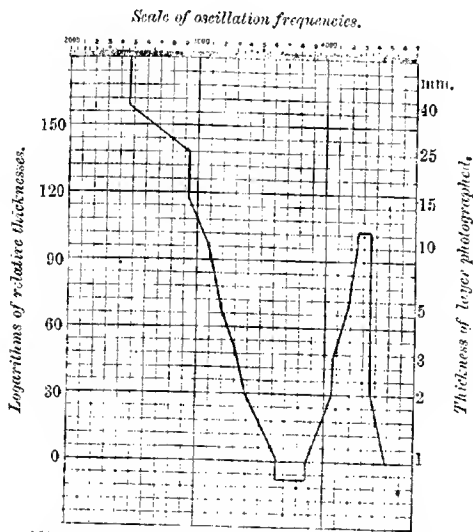
On the addition of potassium chloride to bromine water, the spectra of the solution show one absorption band, and from analogy to the

* An account of the absorption spectra of bromine in various solvents is given in Kayser's *Handbuch der Spectroscopie*, 1905, **3**, 320.

corresponding compounds produced by the addition of a bromide to bromine water, the solution probably contains the ion ClBr_2 . Exactly the same spectra were obtained by the addition of the chlorides of lithium, sodium, rubidium, calcium, strontium, barium, magnesium, cadmium, and aluminium, and also by employing hydrochloric acid, ammonium, tetramethyl- and tetraethyl-ammonium chlorides (Fig. 2).

As in the case of the periodides, the amount of bromine in combination with the bromide or chloride can be approximately determined by comparing the spectra of bromine water containing a small quantity

FIG. 1.

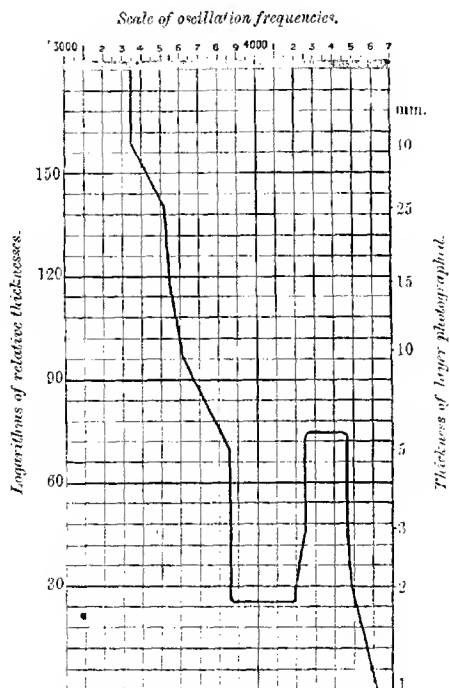


of bromide or chloride with those of bromine water containing excess of the bromide or chloride.

In the latter solutions it may be assumed that the whole of the bromine is in combination with the halogen salt, as when a solution of bromine contains a certain amount of bromide or chloride the addition of more of the salt produces no change in the spectra. In the case of the perbromides, the quantitative determinations by this method of the amount of bromine in combination with a halogen salt are necessarily less accurate than the corresponding determination in the case of the periodides, owing to the rapidity with which the bromine

reacts with the water. A layer 25 mm. thick of an $N/1000$ solution of bromine in water containing 0.24 per cent. of potassium bromide gives spectra which are the same as those of a layer 8 mm. thick of a solution of bromine containing excess of potassium bromide. If, as is probable in the latter case, the whole of the bromine is in combina-

FIG. 2.



tion with the bromide, then in the first solution approximately one-third of bromine is in combination with the bromide.

Similarly, the spectrum of a layer 5 mm. thick of an $N/500$ solution of bromine in water containing 0.5 per cent. of potassium chloride is the same as that of a layer 2 mm. thick of a solution containing excess of potassium chloride. It appears, therefore, that in the solution containing the smaller quantity of potassium chloride, approximately two-fifths of the bromine is in combination with the chloride.

As in the case of iodine, no evidence of the formation of any additive compound of a fluoride and bromine has been obtained.

The view of the formation of additive compounds of bromine with bromides and chlorides receives striking confirmation from the results of determinations of solubility of bromine in solutions of bromides and chlorides.

The solubility of bromine in different solvents is given by McLauchlan (*Zeitsch. physikal. Chem.*, 1903, **44**, 617), Winkler (*Chem. Zeit.*, 1899, **23**, 687), Worley (*Trans.*, 1905, **87**, 1107), and others. From these results it is seen that a normal solution of potassium bromide dissolves approximately four times as much bromine as is dissolved by water, whilst a normal solution of potassium chloride dissolves about one and a-half times as much bromine as is dissolved by water.

Determinations of the solubility of bromine in solutions of magnesium and cadmium bromides and chlorides were also undertaken by the author, and it was found that bromine was much more soluble in the bromide solution than in the corresponding chloride solution. It would be expected, therefore, that by the addition of equivalent quantities of bromide and chloride to similar solutions of bromine, more bromine would combine with the bromide than with the chloride.

It is seen from the spectra that in an *N*/1000 solution of bromine containing 0.24 per cent. of potassium bromide, one-third of the bromine is in combination, whilst in a solution of bromine containing an equivalent quantity of potassium chloride, only about one-tenth of the bromine is in combination.

Alkylsulphine Perbromides.

As in the case of the periodides, the perbromides of the alkylsulphine salts may be represented by one of the following formulæ:



By the addition of trimethylsulphine bromide to bromine water, the solution shows spectra which are exactly the same as those of a solution of bromine containing potassium bromide. Similarly, trimethylsulphine chloride added to bromine water gives a solution the spectra of which are identical with those of a solution of bromine containing potassium chloride.

From these results it would appear that the substances in aqueous solution contain the groups Br_3 and ClBr_2 , so that this affords evidence in favour of formulæ such as (III) for these substances.

It has been shown in the case of the periodides that, in aqueous solution, iodine combined more readily with an iodide than with a bromide, and more readily with a bromide than with a chloride. In the case of the perbromides, it is seen that bromine combines more readily with a bromide than with a chloride. It seemed of interest, therefore, to determine whether a bromide combines more readily with bromine or with iodine, and similarly to find whether a chloride has the greater affinity in aqueous solution for bromine or for iodine.

The results of some preliminary experiments in this connexion may be mentioned. In an $N/1000$ solution of iodine in water containing 0.24 per cent. of potassium bromide, approximately one-third of the iodine is in combination with the bromide.

An $N/1000$ solution of bromine in water containing the same amount of potassium bromide gives spectra which also show that approximately one-third of the bromine is in combination with the bromide.

In the case of equivalent solutions of iodine and bromine containing the same amount of chloride, it appears that the chloride combines more readily with the iodine than with the bromine.

Further experiments in this connexion are being undertaken.

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CLVII.—*The Relation between Unsaturation and Optical Activity. Part IV. The Relative Influence of Bi-, Quadri-, and Sexavalent Sulphur on Rotatory Power.*

By THOMAS PERCY HILDITCH.

THE comparison of various groups of optically active substances containing sulphur has served to show that a bivalent or quadrivalent sulphur atom exerts a greater influence on the optical rotatory power than the more saturated sexavalent sulphur, and, further, that the optical effect is considerably increased if a second group rich in residual affinity is placed adjacent to the unsaturated sulphur atom. Three different series of compounds have been utilised for this purpose, and these will be discussed in the following order:

- (1) Sulphur derivatives of *L*-amyl alcohol.
- (2) " " " camphor.
- (3) Alkaloid salts of aromatic sulphinic and sulphonic acids.

Derivatives of l-Amyl Alcohol.

The following table gives, in addition to the molecular rotation, the algebraic difference between that number and the molecular rotation of *l*-amyl alcohol, in order to display more clearly the influence of the unsaturated groups. Since these sulphur derivatives contain two asymmetric amyl radicles, the "difference" has been estimated by subtracting one-half of the observed molecular rotation from that of *l*-amyl alcohol.

	[M] _D .	Difference.
<i>l</i> -Amyl alcohol, C ₅ H ₁₁ OH	- 4.58	—
Di- <i>l</i> -amyl sulphone, (C ₅ H ₁₁) ₂ SO ₂	about + 34	about 21
Di- <i>l</i> -amyl sulfoxide, (C ₅ H ₁₁) ₂ SO	about + 37	about 23
Di- <i>l</i> -amyl sulphide, (C ₅ H ₁₁) ₂ S	+ 42.67	25.91
Di- <i>l</i> -amyl disulphide, (C ₅ H ₁₁) ₂ S ₂ (C ₅ H ₁₁) ₂ ..	+ 149.40	79.28

The di-*l*-amyl sulphone and sulfoxide were prepared according to the methods described by Saytzeff (*Annalen*, 1866, **139**, 354) and Beckmann (*J. pr. Chem.*, 1878, [ii], **17**, 440), but, as the diamyl sulphide used in the preparation was unfortunately not optically pure, the figures are given only as some rough indication of the true values. The data for diamyl sulphide and disulphide are taken from Brjuchonenko's figures (*J. pr. Chem.*, 1899, [ii], **59**, 47, 596). In this series, a simple decrease in valency of the sulphur seems to be accompanied by small increase in optical activity, but when two bivalent sulphur atoms occur in conjugation, an extraordinary optical exaltation occurs, and this behaviour finds a striking parallel in the similar cases of camphor derivatives quoted below.

*Derivatives of d-Camphor.**

A comparison of some substances related to camphor- β -sulphonic acid is still more instructive :

	[M] _D .	Difference.
<i>d</i> -Camphor, C ₁₅ H ₁₆ O	+ 63	—
<i>d</i> -Camphor- β -sulphonic acid, C ₁₅ H ₁₅ O \cdot SO ₂ OH	+ 49	19
<i>d</i> -Camphor- β -sulphonyl chloride, C ₁₅ H ₁₅ O \cdot SO ₂ Cl	+ 78	10
<i>d</i> -Diacamporyl β - α -disulphone, C ₁₅ H ₁₅ O \cdot SO ₂ \cdot SO ₂ \cdot C ₁₅ H ₁₅ O ..	+ 132	2
<i>d</i> -Camphor- β -sulphinic acid, C ₁₅ H ₁₅ O \cdot SO ₂ H	- 157	225
<i>d</i> -Camporyl- β -mercaptan, C ₁₅ H ₁₅ O \cdot SH	+ 11	57
<i>d</i> -Camporyl- β -mercaptan acetate, C ₁₅ H ₁₅ O \cdot S \cdot CO \cdot CH ₃	- 93	161
<i>d</i> -Camporyl- β -mercaptan benzoate, C ₁₅ H ₁₅ O \cdot S \cdot CO \cdot C ₆ H ₅	- 46	114
<i>d</i> -Diacamporyl β -disulphide, C ₁₅ H ₁₅ O \cdot S ₂ \cdot C ₁₅ H ₁₅ O	- 355	246

Reviewing these in detail, it is seen that the sulphonyl chloride and disulphone contain the most "saturated" sulphur nuclei, and that

* The references from which these figures are collected are: camphor- β -sulphonic acid, Reychler, *Bull. Soc. chim.*, 1898, [iii], **19**, 120; camphor- β -sulphonyl chloride, Armstrong and Lowry, *Trans.*, 1902, **81**, 1417; camporyl- α -disulphone and - β -sulphinic acid, Smiles and Hilditch, *Trans.*, 1907, **91**, 519; camporyl- β -mercaptan and its derivatives, Lowry and Donnington, *Trans.*, 1903, **83**, 479.

these possess optical activity of much the same order as camphor itself. On the other hand, in the sulphonic acid, there exists contiguous to the sulphone residue a hydroxyl group possessing some degree of residual affinity, and corresponding with this a change of about twenty degrees takes place in the molecular rotation. Camphor- β -sulphinic acid, presumably containing quadrivalent sulphur, shows a very pronounced alteration in activity, far greater even than that of the mercaptan; it has been pointed out (Smiles and Hilditch, *loc. cit.*) that there can be no other possible change in constitution accompanying the transition from sulphonic to sulphinic acid unless the enolic structure were present in camphorsulphinic acid, and the latter supposition is at present unsubstantiated by any chemical evidence. Hence it must be supposed that the large change in rotatory power is due to the increased unsaturation of the sulphur caused by decrease of valency, and to the conjunction of the quadrivalent sulphur with the hydroxyl group. Other quadrivalent sulphur compounds, such as diphenetylcamphorylsulphonium derivatives, also show a large negative molecular rotation, but, as these are exceedingly complicated and of much larger molecular weight, it is not advisable to draw many conclusions from them.

Finally, a well-marked regularity may be observed in the bivalent thio-derivatives of camphor. Camphor- β -mercaptan shows a difference of 57° from the molecular rotatory power of camphor, and, further, when other unsaturated groups are placed adjacent to the sulphur atom, as in the acetate and benzoate, this difference is doubled or trebled. Most remarkable of all is the change observed when two bivalent sulphur atoms are conjugated; here the alteration is more than four times as great as for the mercaptan, a difference which is strictly parallel with the relations between diamyl disulphide and sulphide quoted on a previous page. On the other hand, the rotation of camphoryl β - α -disulphone affords a contrast to this behaviour, for in this instance there are two relatively saturated sulphone groups in conjugation, and no optical anomaly whatever is observed. It is also noticeable that the very enhanced change in rotation in the cases of diamyl and dicamphoryl disulphides occurs where the conjugated unsaturated groups are identical and symmetrically arranged.

It should be stated that the optical activity of all the above substances was measured in alcohol or, in a few cases, in chloroform solution.

Alkaloid Salts of Aromatic Sulphinic and Sulphonic Acids.

The study of brucine and cinchonine salts of some corresponding sulphinic and sulphonic acids has furnished results leading to con-

clusions which at a first glance seem opposed to those drawn from the above instances. The acids used have been in every case members of the aromatic series, and so, judging from previous experience, one might expect any change due to unsaturation in the acidic group to be reinforced by the presence of the contiguous benzenoid residue. The salts were prepared and purified by the same methods as had been previously used (Parts II and III of this series, *Trans.*, 1908, **93**, 700, 1388), and were examined in the polariscope in chloroform solution at two dilutions, namely, 5 and $2\frac{1}{2}$ per cent. The measurements were made in a 2-dm. tube at a temperature of 21° , except in the cases specially indicated, and the figures obtained, which, together with the optical rotatory powers of the parent alkaloids, are collected in the following tables, show that a sulphonic acid has in general a greater effect than the corresponding sulphinic acid on the optical activity of the base.

I. *Brucine Salts.*

Percentage concentration : Acid.	5		$2\frac{1}{2}$	
	$[\alpha]_D$	$[M]_D$	$[\alpha]_D$	$[M]_D$
(Benzenesulphinic *	- 122.0	- 480.7	- 122.0	- 480.7
{ Benzenesulphonic *	- 19.8	- 106.1	- 20.2	- 108.2
{ <i>p</i> -Toluenesulphinic	16.1	88.9	16.6	91.6
{ <i>p</i> -Toluenesulphonic	15.2	83.6	15.0	82.5
{ <i>p</i> -Xylene-2-sulphinic	12.5	70.7	11.8	66.8
{ <i>p</i> -Xylene-2-sulphonic	14.0	79.0	14.2	80.1
{ <i>p</i> -Phenetylsulphinic *	15.5	89.9	16.0	92.8
{ <i>p</i> -Phenetylsulphonic *	20.3	117.7	20.2	117.1
{ <i>p</i> -Phenetylsulphonic *	14.1	84.0	14.2	84.6

* Temperature = 22° .II. *Cinchonine Salts.*

Percentage concentration : Acid.	5		$2\frac{1}{2}$	
	$[\alpha]_D$	$[M]_D$	$[\alpha]_D$	$[M]_D$
{ Benzenesulphinic..... ..	+ 222.0	+ 652.7	+ 222.0	+ 652.7
{ Benzenesulphonic	+ 111.4 *	+ 485.6	+ 123.6	+ 538.9
{ <i>p</i> -Toluenesulphinic	90.2 *	407.7	90.6	409.5
{ <i>p</i> -Toluenesulphonic	100.3	451.4	107.6	481.2
{ <i>p</i> -Xylene-2-sulphinic	94.9	442.3	99.0	461.3
{ <i>p</i> -Xylene-2-sulphonic	114.2	529.9	120.2	557.7
{ <i>p</i> -Phenetylsulphinic	97.2	466.6	103.8	498.0
{ <i>p</i> -Phenetylsulphonic	101.2	485.6	104.2	500.0
{ <i>p</i> -Phenetylsulphonic	98.1	486.6	105.4	522.9

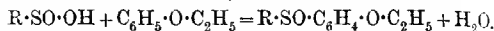
* Temperature = 23° .

The interpretation of these results depends on the constitution assigned to the salts of aromatic sulphinic acids. It is generally assumed that, at all events, the free acids contain quadrivalent sulphur, for the following reasons.

(1) As a class they do not possess the stability usually associated with compounds containing the sexavalent sulphono residue.

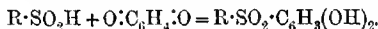
(2) On esterification with alcohols and hydrogen chloride, esters are formed isomeric with, but distinct from, the alkyl sulphones (Otto, *Ber.*, 1885, **18**, 2493).

(3) In concentrated sulphuric acid solution, sulfoxides or sulphonium bases may be formed by condensation (Smiles and Le Rossignol, *Trans.*, 1906, **89**, 706):



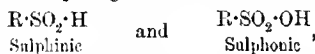
On the other hand, the following reactions indicate that under suitable conditions a portion at least of the acid exists in the form $R \cdot SO_2 \cdot H$ and contains sexavalent sulphur.

(1) Substituted sulphones result from the union of sulphinic acids with quinone derivatives (Hinsberg and Himmelschein, *Ber.*, 1896, **29**, 2024):



(2) The author (*Trans.*, 1908, **93**, 1524) has recently shown that in glacial acetic acid solution part of the acid is converted on oxidation to α -disulphone.

Again, practically all the reactions of the sodium salts of these acids accord better with the sexavalent than with the quadrivalent sulphur formula. Thus with alkyl iodides, sulphones and not sulphinic esters are formed (Otto, *Ber.*, 1880, **13**, 1272), whilst aromatic α -disulphones result by their interaction with aromatic sulphonyl chlorides (Köhler and MacDonald, *Amer. Chem. J.*, 1899, **22**, 224). There are therefore good reasons for inferring that the alkaloid sulphinates contain the sulphinic acid in the sexavalent form $R \cdot SO_2 \cdot H$, rather than in the quadrivalent, $R \cdot SO \cdot OH$, a conclusion which is supported by the difficult fusibility and the stability at high temperatures of most of the salts described. Comparing the two series of salts from



it is evident that in those of the sulphonic series the sulphone group is associated with the unsaturated hydroxyl, whilst in the sulphinic salts the sulphone nucleus is united to hydrogen, an element which may be considered to be completely saturated. The optical behaviour, therefore, falls into line with all the other cases to which allusion has been made, and it may be said that the effect of a relatively unsaturated sulphur atom in an optically active compound is to cause an abnormal rotatory power, and is of a similar nature to that of other types of unsaturation previously examined.

EXPERIMENTAL.

1-Diamyl Sulphoxide, $(C_5H_{11})_2SO$.

About 20 grams of *l*-diamyl sulphide were dropped in small portions at a time into a large excess of cold fuming nitric acid. After the first vigorous action had subsided, the mixture was set aside for a few minutes, and then poured into a large bulk of water (Saytzeff, *loc. cit.*). The sulphoxide separated as an oil which quickly solidified; after recrystallisation from light petroleum it formed short, colourless, waxy prisms, melting at 40° :

0.1108 gave 0.2563 CO_2 and 0.1147 H_2O . $C = 63.09$; $H = 11.50$.

$C_{10}H_{22}OS$ requires $C = 63.16$; $H = 11.58$ per cent.

1-Diamyl Sulphone, $(C_5H_{11})_2SO_2$.

The sulphoxide was oxidised by excess of powdered potassium permanganate in glacial acetic acid solution in the cold. After dilution with water and removal of the excess of permanganate with sulphurous acid, the product solidified. On crystallisation from light petroleum it separated in long, colourless needles, which melted at $29-30^\circ$:

0.2785 gave 0.5922 CO_2 and 0.2607 H_2O . $C = 57.98$; $H = 10.40$.

$C_{10}H_{22}O_2S$ requires $C = 58.25$; $H = 10.68$ per cent.

Brucine Salts.

Brucine Benzenesulphinate, $C_{23}H_{26}O_4N_2 \cdot C_6H_5 \cdot SO_2H \cdot 2H_2O$.—Cream-coloured, cubical crystals, melting and decomposing at 209° :

0.1548 gave 0.3438 CO_2 and 0.0912 H_2O . $C = 60.56$; $H = 6.55$.

$C_{29}H_{32}O_6N_2S \cdot 2H_2O$ requires $C = 60.84$; $H = 6.29$ per cent.

Brucine Benzenesulphonate, $C_{23}H_{26}O_4N_2 \cdot C_6H_5 \cdot SO_3H \cdot 6\frac{1}{2}H_2O$.—A very deliquescent, cream-coloured powder, sparingly soluble in alcohol or chloroform and insoluble in acetone, loses water at $100-105^\circ$, and melts at 207° :

0.1215 gave 0.2319 CO_2 and 0.0735 H_2O . $C = 52.06$; $H = 6.72$.

$C_{29}H_{32}O_7N_2S \cdot 6\frac{1}{2}H_2O$ requires $C = 52.02$; $H = 6.73$ per cent.

Brucine p-Toluenesulphinate, $C_{23}H_{26}O_4N_2 \cdot C_7H_7 \cdot SO_3H$.—Large, white prisms, fairly soluble in alcohol, melting and decomposing at $240-245^\circ$:

0.1052 gave 0.2531 CO_2 and 0.0583 H_2O . $C = 65.61$; $H = 6.16$.

$C_{30}H_{34}O_6N_2S$ requires $C = 65.45$; $H = 6.18$ per cent.

Brucine p-Toluenesulphonate, $C_{23}H_{26}O_4N_2 \cdot C_7H_7 \cdot SO_3H \cdot 2\frac{1}{2}H_2O$.—

Slender leaflets, melting at 115—116°, resolidifying and undergoing no further visible change below 230°:

0.1457 gave 0.3160 CO₂ and 0.0855 H₂O. C = 59.14; H = 6.52.

C₃₀H₃₄O₇N₂S₂·2½H₂O requires C = 58.92; H = 6.38 per cent.

Brucine p-Xylene-2-sulphinat, C₂₂H₂₆O₄N₂·C₈H₈·SO₂H₂·2H₂O.—A white, microcrystalline powder, sparingly soluble in water, readily so in alcohol, melting and slightly decomposing at 223°:

0.1574 gave 0.3588 CO₂ and 0.0942 H₂O. C = 62.18; H = 6.65.

C₃₁H₃₆O₆N₂S₂·2H₂O requires C = 62.00; H = 6.67 per cent.

Brucine p-Xylene-2-sulphonat, C₂₂H₂₆O₄N₂·C₈H₈·SO₃H₂·2H₂O.—A white, microcrystalline powder, sparingly soluble in water, melting at 180°:

0.1515 gave 0.3374 CO₂ and 0.0911 H₂O. C = 60.73; H = 6.68.

C₃₁H₃₆O₇N₂S₂·2H₂O requires C = 60.39; H = 6.49 per cent.

Brucine p-Phenylsulphinat, C₂₂H₂₆O₄N₂·C₆H₅·SO₂H₂·1½H₂O.—Very small needles, softening indefinitely at 215—220°:

0.1888 gave 0.4252 CO₂ and 0.1086 H₂O. C = 61.41; H = 6.39.

C₃₁H₃₆O₇N₂S₂·1½H₂O requires C = 61.28; H = 6.43 per cent.

Brucine p-Phenylsulphonat, C₂₂H₂₆O₄N₂·C₆H₅·SO₃H₂·2½H₂O.—Compact, white tablets, melting and losing water at 116—117°, then resolidifying and remaining unfused at 260°:

0.1096 gave 0.2339 CO₂ and 0.0615 H₂O. C = 58.20; H = 6.24.

C₃₁H₃₆O₈N₂S₂·2½H₂O requires C = 58.02; H = 6.40 per cent.

Cinchonine Salts.

Cinchonine Benzenesulphinat, C₁₉H₂₂ON₂·C₆H₅·SO₂H₂·C₆H₅O.—Small, white needles precipitated from alcohol by ether, sparingly soluble in water, melting and decomposing at 214°:

0.1500 gave 0.3682 CO₂ and 0.0942 H₂O. C = 66.92; H = 6.38.

C₂₅H₂₅O₃N₂S₂·C₆H₅O requires C = 67.22; H = 7.05 per cent.

Cinchonine Benzenesulphonat, C₁₉H₂₂ON₂·C₆H₅·SO₃H₂·6½H₂O.—White, deliquescent prisms, very soluble in water, sparingly so in chloroform, decomposing indefinitely at 105—110°:

0.1180 gave 0.2291 CO₂ and 0.0731 H₂O. C = 52.94; H = 6.88.

C₂₂H₂₈O₄N₂S₂·6½H₂O requires C = 52.72; H = 7.21 per cent.

Cinchonine p-Toluenesulphinat, C₁₉H₂₂ON₂·C₇H₇·SO₂H₂·H₂O.—Very small prisms, sparingly soluble in cold water, melting at 198°:

0.1043 gave 0.2565 CO₂ and 0.0641 H₂O. C = 67.07; H = 6.83.

C₂₆H₃₀O₃N₂S₂·H₂O requires C = 66.68; H = 6.84 per cent.

Cinchonine p-Toluenesulphonat, C₁₉H₂₂ON₂·C₇H₇·SO₃H₂·4½H₂O.—

Deliquescent scales, melting indefinitely at 70—75°, resolidifying above 100°:

0.1816 gave 0.3808 CO₂ and 0.1100 H₂O. C = 57.19; H = 6.73.

C₂₆H₃₀O₄N₂S₂·4½H₂O requires C = 57.05; H = 7.13 per cent.

Cinchonine p-Xylene-2-sulphinat, C₁₀H₂₂ON₂·C₈H₈·SO₂H₂·3H₂O.—Thin, white leaflets, sparingly soluble in water or alcohol, evolving water and melting indefinitely from 115—120°:

0.1948 gave 0.4438 CO₂ and 0.1298 H₂O. C = 62.12; H = 7.40.

C₂₇H₃₂O₈N₂S₂·3H₂O requires C = 62.55; H = 7.34 per cent.

Cinchonine p-Xylene-2-sulphonat, C₁₀H₂₂ON₂·C₈H₈O·SO₃H₂·2½H₂O.—Long, white needles, somewhat sparingly soluble in water, melting and evolving water at 110°:

0.1300 gave 0.2940 CO₂ and 0.0861 H₂O. C = 61.67; H = 7.39.

C₂₇H₃₂O₄N₂S₂·2½H₂O requires C = 61.70; H = 7.05 per cent.

Cinchonine p-Phenylsulphinat, C₁₀H₂₂ON₂·C₈H₈O·SO₂H₂·C₆H₅O.—Clusters of long, slender needles, darkening at 225—230°:

0.1123 gave 0.2716 CO₂ and 0.0711 H₂O. C = 65.97; H = 7.04.

C₂₇H₃₂O₄N₂S₂·C₆H₅O requires C = 66.16; H = 7.22 per cent.

Cinchonine p-Phenylsulphonat, C₁₀H₂₂ON₂·C₈H₈O·SO₃H₂·4½H₂O.—An exceedingly deliquescent powder, moderately soluble in chloroform:

0.1552 gave 0.3184 CO₂ and 0.0958 H₂O. C = 55.98; H = 6.86.

C₂₇H₃₂O₅N₂S₂·4½H₂O requires C = 56.14; H = 7.11 per cent.

The author's thanks are tendered to Assistant-Professor Smiles for much helpful criticism.

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CLVIII.—Coprosterol. Part I.

By CHARLES DORÉE and JOHN ADDYMAN GARDNER.

IN 1862 Austen Flint, jun., in the course of an investigation in which he attempted to show that cholesterol is a product of the metabolism of nervous tissue which is excreted through the bile, isolated from human faeces a cholesterol-like substance to which he gave the name of stercorine. This, under the name of coprosterol, was again

described in 1896 by Bondzynski (*Ber.*, 1896, 29, 476), and was carefully examined by Bondzynski and Humnicki (*Zeitsch. physiol. Chem.*, 1896, 22, 396). They showed that it was an alcohol, yielding characteristic derivatives; that it was saturated towards bromine, and that it gave the cholesterol colour reactions in a modified form. As a result of their analyses, they assigned to it the formula $C_{27}H_{48}O$, and regarded it as a dihydrocholesterol formed by bacterial reduction in the intestines. This view was supported by their observation that cholesterol given by the mouth appeared in the faeces as coprosterol. That coprosterol is produced by a bacterial action in the gut was rendered still more probable by the work of Müller (*Zeitsch. physiol. Chem.*, 1900, 29, 129), who found that on a prolonged milk diet, in the course of which putrefactive changes in the intestine are reduced to a minimum, cholesterol only was excreted in the faeces and no coprosterol. Our own observations (*Proc. Roy. Soc.*, 1908, 80, B, 212, 228) have made it clear that neither cholesterol nor a derived product is ever found in the faeces of herbivorous animals, unless administered as such, in which case it is passed unchanged. In the case of carnivorous animals, such as the dog and the cat, we found that the faeces normally contain small quantities of cholesterol, but that on a diet of raw brain, which contains some $2\frac{1}{2}$ per cent. of its weight of cholesterol, this substance is entirely converted during its passage through the intestine into coprosterol. This discovery enables us to obtain pure coprosterol in considerable quantity. Thus in fourteen days a dog consumed 2 kilos. of brain and produced 17 grams of coprosterol. The output of the human subject on normal diet is very small, in our experience rarely amounting to more than 0.25 gram per day, and it is accompanied by a red, unsaponifiable oil, which makes its purification very difficult. Bondzynski and Humnicki made numerous attempts to convert cholesterol into coprosterol *in vitro* by the action of various bacteria, but without success. Our own series of experiments, using *B. coli communis*, also led to negative results.

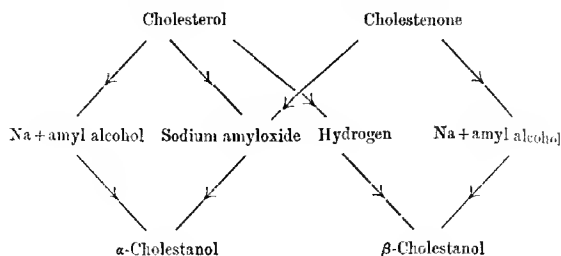
The physiological importance of these substances, and the explanation that had been given of their relationship, has led to various attempts being made to settle the question by studying the reduction of cholesterol by chemical means. The unsaturated linking of cholesterol is, however, not readily reduced by the ordinary agents. In 1904 C. Neuberg (Salkowski, *Festschrift*, 1904, 279) stated that, by the action of sodium in boiling amyl-alcoholic solution, he had succeeded in reducing cholesterol, and that among the products of the action he had found coprosterol. He had, in fact, obtained a saturated alcohol apparently of the formula $C_{27}H_{48}O$, melting between 124° and 126° . The difference between this melting point

and the 95° attributed to natural coprosterol, he explained by the statement that Bondzynski's product was not a single substance. By repeated crystallisation of a sample from human faeces, Nenberg was able to raise the melting point to 99–100°, and suggested that by suitable purification it would be possible to raise the melting point still further, until it approached that of his artificial product. We can confirm the fact that the melting point of coprosterol is 99–100° (*loc. cit.*), but we were unable after elaborate crystallisation to raise it above this, and, when coprosterol was regenerated from highly purified esters, its melting point remained unaltered. The action of sodium and amyl alcohol on cholesterol was again examined in 1906 by Diels and Abderhalden (*Ber.*, 1906, 39, 884), who obtained a crystalline compound which sintered at 118° and melted at 124–126°, and characterised it as a saturated secondary alcohol of the formula $C_{27}H_{48}O$. This substance they named α -cholestanol, and considered it to be dihydrocholesterol.

On the other hand, Windaus (*Ber.*, 1907, 40, 2637) obtained the same compound by the action of sodium amyloxide, and therefore gave it as his opinion that α -cholestanol was not a reduction product, but was produced by the linking up of the unsaturated side-chain of cholesterol with the formation of a new ring in a manner analogous to that of the condensation of the olefinic terpenes to cyclic terpenes, and proposed to call it *cyclocholesterol*.

In the paper referred to above, Diels and Abderhalden also showed that cholestenone, on treatment with sodium in amyl-alcoholic solution, was reduced to a saturated secondary alcohol of the formula $C_{27}H_{48}O$, which was not identical with that obtained from cholesterol. This β -cholestanol, as it was called, melts at 143°, and gives a ketone melting at 129°. That this substance is the normal dihydrocholesterol has recently been clearly shown by R. Willstätter, who obtained it in a practically quantitative yield by the reduction of cholesterol in ethereal solution with hydrogen in the presence of platinum-black (*Ber.*, 1908, 41, 2199).

This observation makes the hypothesis of Windaus as to the relationship of cholesterol and α -cholestanol a very probable one, more especially as Diels and Linn (*Ber.*, 1908, 41, 554) have proved that the two compounds are not geometrical isomerides, since two different cholestanes can be obtained from them. The same authors have, however, shown that sodium amyloxide can act as a reducing agent, since cholestenone under its influence gives α -cholestanol, so that apparently reduction and condensation in this case take place simultaneously. These relationships may be summarised in the following scheme:



Diels and Linn further showed (*Ber.*, 1908, 41, 260) that when cholesterol is heated to 300° in the presence of a trace of iron salt, cholestenone is produced, together with an isomeride of cholesterol, which they called β -cholesterol. This yields a dibromide and esters identical with those of cholesterol itself. It was also obtained by the reduction of cholestenone with sodium and ethyl alcohol, so that this reagent does not appear to act on the unsaturated linking of cholestenone. β -Cholesterol, when heated with sodium and amyl alcohol, however, gives α -cholestanol.

It will be apparent from these results that no derivative resembling coprosterol has so far been obtained from cholesterol by the action of the reducing or isomerising agents hitherto tried. It seemed to us, therefore, desirable to attack the problem from the other side, and to study the action of oxidising agents, and also of sodium amyloxide, on natural coprosterol in order to ascertain whether any of the products so obtained were identical with those formed from cholesterol. We find that coprosterol is readily oxidised on treatment with the theoretical quantity of chromic acid, with the production of the corresponding ketone, *coprostanone*. Under the influence of sodium amyloxide, coprosterol is converted into an isomeric substance, which we name for the present ψ -*coprosterol*. The esters of this compound are different from those of coprosterol, but on oxidation with chromic acid it yields the same ketone, *coprostanone*.

EXPERIMENTAL.

Coprostanone.

Ten grams of coprosterol were dissolved in 70 c.c. of glacial acetic acid, and a solution of 2.8 grams of chromic anhydride in a little dilute acetic acid poured in. On standing in the cold, the liquid soon became bluish-grey in colour, and, on warming to 50°, rapidly turned green. The oxidation was finished by heating for an hour on the water-bath. The solution, after cooling, was diluted somewhat with

water, which precipitated the ketone as a sticky solid. This was removed by extraction with ether, the ethereal solution being washed with water and alkali, dried, and allowed to evaporate. The white solid obtained was somewhat soluble in the usual solvents, but by dissolving it in a mixture of acetone (1 part) and alcohol (3 parts), and allowing it to evaporate at the ordinary temperature, it crystallised well. The yield of pure product was 60 per cent.

Coprostanone crystallises in beautiful glistening leaves, and, under the microscope, appears in the form of very thin plates, generally square, with one or all of the corners slightly truncated. It melts at $62-63^{\circ}$ to a clear liquid. When treated with a solution of bromine in carbon disulphide, it rapidly absorbs bromine. This unexpected result is similar to one observed by Willstätter and Mayer (*Ber.*, 1908, 41, 2199), who found that the ketone obtained from the saturated β -cholestanol by simple oxidation likewise absorbed bromine. For analysis, the body was dried in a vacuum:

0.2319 gave 0.7132 CO_2 and 0.2478 H_2O . $\text{C}=83.87$; $\text{H}=11.86$.

$\text{C}_{27}\text{H}_{46}\text{O}$ requires $\text{C}=83.91$; $\text{H}=11.92$ per cent.

Coprostanone semicarbazone.—One gram of the ketone dissolved in alcohol was mixed with a solution of 0.3 gram of semicarbazide hydrochloride in water and 0.22 gram of sodium acetate in alcohol. The clear solution soon became full of white clots, and was allowed to stand for three days, when the organic matter was precipitated by the addition of water. The white powder obtained was insoluble in ether and light petroleum, and was boiled out with these solvents. From benzene, it separated in masses, but was not apparently crystalline. It was purified by solution in benzene and precipitation by light petroleum. On slow heating, it shrinks at 187° , melts at 192° , and decomposes above 195° . For analysis, it was dried at 100° and in a vacuum:

0.1802 gave 0.5002 CO_2 and 0.1854 H_2O . $\text{C}=75.70$; $\text{H}=11.43$.

0.1805 „ 0.5041 CO_2 „ 0.1814 H_2O . $\text{C}=76.16$; $\text{H}=11.16$.

0.1825 „ ——— CO_2 „ 0.1843 H_2O . $\text{C}=$ —; $\text{H}=11.00$.

0.1978 „ 15.6 c.c. N_2 (moist) at 16° and 759 mm. $\text{N}=9.19$.

$\text{C}_{28}\text{H}_{44}\text{ON}_3$ requires $\text{C}=76.11$; $\text{H}=10.73$; $\text{N}=9.54$ per cent.

Phenylhydrazine compound.—With phenylhydrazine, the ketone reacts readily, but gives an abnormal derivative. Two grams of coprostanone were dissolved in 40 c.c. of glacial acetic acid, and the calculated quantity of the base (freshly distilled), dissolved in strong acetic acid, added to the solution. The liquid was warmed at 40° and shaken for fifteen minutes, when the action suddenly set in and a copious, yellow precipitate was formed. After some time, this was

collected, washed with dilute acetic acid and water, and dried. Yield, about 50 per cent.

The substance is almost insoluble in absolute alcohol and light petroleum, which were used to remove colour. The very pale ochre-coloured residue was then dissolved in a little warm benzene, and the solution mixed with an excess of alcohol. On cooling, small, white, glancing crystals were formed, which had a needle-like appearance, but under the microscope were seen to consist of very long, rectangular plates. These melt to a red liquid at 192° without apparent decomposition. For analysis, the substance was dried at 100° and in a vacuum:

0.1595	gave	0.5080 CO_2	and	0.1557 H_2O .	C = 86.86; H = 10.86.
0.1599	"	0.5057 CO_2	"	0.1524 H_2O .	C = 86.25; H = 10.59.
0.0934	"	0.2973 CO_2	"	0.0952 H_2O .	C = 86.81; H = 11.32.
0.1587	"	0.5034 CO_2	"	0.1555 H_2O .	C = 86.51; H = 10.88.
0.2213	"	6.15 c.c. N_2	(moist) at 18°	and 763 mm.	N = 3.22.
0.1772	"	5.7 c.c. N_2	"	" 19° "	760 mm. N = 3.70.

The normal phenylhydrazone, $\text{C}_{27}\text{H}_{46}\cdot\text{N}_2\text{H}\cdot\text{C}_6\text{H}_5$, requires C = 83.19; H = 10.93; N = 5.68 per cent. A substance of the formula $\text{C}_{26}\text{H}_{46}\text{C}\cdot\text{N}\cdot\text{C}_6\text{H}_5$ would require C = 85.9; H = 11.0; N = 3.1, but we are not at present able to throw any light on the composition of this compound. It may be mentioned that it is also formed, although in a poor yield, by boiling the ketone with phenylhydrazine.

Coprostanoneoxime.—One gram of the ketone in 15 c.c. of absolute alcohol was mixed with a warm solution of 0.5 gram of hydroxylamine hydrochloride in dilute alcohol, and 0.5 gram of sodium hydroxide, in a little water, added. After boiling for two hours, the cooled liquid was poured into water, when the oxime separated as a white powder, which was collected and dried at a low temperature. It was readily soluble in all solvents except ethyl and methyl alcohol, and could not be made to crystallise. It was therefore repeatedly extracted with warm methyl alcohol, and dried in a vacuum, when it became brittle and easily powdered. On heating, it softened at 69° and melted at 71° , decomposing at 80° . For analysis, it was dried in a vacuum:

0.1770	gave	0.5208 CO_2	and	0.1880 H_2O .	C = 80.25; H = 11.81.
0.2365	"	7.7 c.c. N_2	(moist) at 18°	and 768 mm.	N = 3.81.
$\text{C}_{27}\text{H}_{46}\text{ON}$ requires C = 80.70; H = 11.72; N = 3.50 per cent.					

The Action of Sodium Amylozide on Coprosterol.

ψ -Coprosterol.—Twenty grams of sodium were dissolved in 400 c.c. of boiling amyl alcohol, 20 grams of coprosterol added, and the mixture boiled for eight hours. The liquid was then cautiously treated with water, the amyl alcohol layer removed, and washed with

water and dilute acid. The alcohol was then distilled off in steam, being removed as completely as possible, and the horny mass remaining in the flask was collected and dried. The solid was crystallised first from acetone, which removes oily matter, and then from dilute or absolute alcohol. Yield, 60 per cent.

ψ -Coprosterol crystallises from dilute ethyl or methyl alcohol in long, pointed needles which form prickly clusters, and from acetone in masses of fine, felted needles. It is readily soluble in ethyl acetate, benzene, or chloroform, and moderately so in light petroleum, from which it was finally purified, as coprosterol is very soluble in this solvent. A sample was crystallised three times each from alcohol, acetone, and light petroleum. It softened at $115-116^\circ$ and melted at 119° . It was saturated towards bromine in carbon disulphide solution, and was dextrorotatory:

0.84 gram, made up to 25 c.c. with chloroform, gave $\alpha + 2.12^\circ$ in a 2-dm. tube, hence $[\alpha]_D^{20} + 31.55^\circ$.

On analysis, after drying at 100° and in a vacuum:

0.1588 gave 0.4842 CO_2 and 0.1688 H_2O . C = 83.12; H = 12.51.

0.1829 „ 0.5605 CO_2 „ 0.2023 H_2O . C = 83.58; H = 12.29.

$\text{C}_{27}\text{H}_{48}\text{O}$ requires C = 83.51; H = 12.36 per cent.

It gave the cholesterol colour reactions in a modified way. When a chloroform solution was mixed with an equal bulk of concentrated sulphuric acid, the upper layer alone became pale yellow. When a saturated solution in cold acetic anhydride was mixed with concentrated sulphuric acid, a brown ring appeared, and the upper layer of liquid became first blue and then green, whilst in half a minute the whole mass of the liquid became brown.

The secondary alcoholic nature was shown by the preparation of the following derivatives:

ψ -Coprosterol Acetate.—The substance was boiled for twenty minutes with acetic anhydride, and the liquid poured into water. The acetate is very soluble in most solvents, but readily crystallises from absolute alcohol in minute, nodular, or prism-shaped crystals, which are hard and gritty and melt at $83-84^\circ$. On analysis:

0.1711 gave 0.5066 CO_2 and 0.1805 H_2O . C = 80.71; H = 11.66.

0.1564 „ 0.4629 CO_2 „ 0.1642 H_2O . C = 80.72; H = 11.67.

$\text{C}_{29}\text{H}_{50}\text{O}_2$ requires C = 80.93; H = 11.63 per cent.

ψ -Coprosterol Benzoate.—This ester is not formed by the use of pyridine and benzoyl chloride as in the case of coprosterol (Dorée and Gardner, *loc. cit.*). One gram of the substance was mixed with 3 c.c. of benzoyl chloride, and heated at 150° for two hours. After some time, the benzoyl chloride was distilled off in a vacuum. The oily residue was very difficult to crystallise. It was extracted several

times with methyl alcohol, dissolved in ether, and mixed with alcohol. Clear oil drops were then deposited, which soon solidified to masses of needle-like plates, melting at 85–86°. It is very soluble in acetone, benzene, or light petroleum. On analysis :

0.1681 gave 0.5098 CO_2 and 0.1629 H_2O . $\text{C} = 82.71$; $\text{H} = 10.76$.

$\text{C}_{34}\text{H}_{52}\text{O}_2$ requires $\text{C} = 82.93$; $\text{H} = 10.58$ per cent.

Both the acetate and benzoate of ψ -coprosterol are saturated towards bromine.

Oxidation to a Ketone.—When treated with the theoretical amount of chromic acid in glacial acetic acid solution, ψ -coprosterol was readily attacked. The product proved to be a ketone identical in every respect with coprostanone. The crystalline form and melting point were the same, and it readily absorbed bromine. The semicarbazone and the phenylhydrazine compound were prepared, and in melting point and other properties were in complete agreement with the corresponding derivatives of coprostanone. The phenylhydrazine compound, on analysis, gave the following figures :

0.1237 gave 0.3936 CO_2 and 0.1255 H_2O . $\text{C} = 86.78$; $\text{H} = 11.27$.

0.1255 „ 3.95 c.c. N_2 (moist) at 21° and 768 mm. $\text{N} = 3.7$.

The isomerism of coprosterol and ψ -coprosterol would therefore seem to be due to the position of the hydroxyl group with regard to the ring plane.

Conclusions.

1. The formation of coprostanone shows that coprosterol, like cholesterol, is a secondary alcohol, and our analyses do not disagree with the formula $\text{C}_{37}\text{H}_{58}\text{O}$ assigned to it by Bondzynski and Humnicki; but neither coprosterol nor its derivatives correspond with any of the products obtained by the action of reducing or isomerising agents on cholesterol, as will appear from the following table :

Alcohol, $\text{C}_{37}\text{H}_{58}\text{O}$.	M. p.	Acetate. m. p.	Benzoate. m. p.	Ketone. m. p.
α -Cholestanol.....	126°	—	129°	119°
β -Cholestanol.....	143	110°	—	129
Coprosterol.....	100	88	122	63
ψ -Coprosterol.....	119	81	85	63

so that the relationship of the two substances still remains uncertain.

2. The above results show that coprosterol is not formed from cholesterol by a simple addition of hydrogen to the double linking, as previously supposed.

3. Whether coprosterol is a reduction product of cholesterol which has simultaneously undergone structural change or whether it is a saturated isomeride of that compound cannot be definitely stated, as the combustion method does not enable us to decide between small

differences in the number of hydrogen atoms. We do not consider it unlikely that coprosterol may have a lower carbon content than cholesterol, and may be produced by the elimination of a carbon atom under bacterial influence. The analytical figures agree in most cases equally well with a C_{26} or a C_{27} formula. This question we hope to solve by a study of the oxidation products of coprosterol.

The expenses of this investigation were covered by a grant from the Government Grant Committee of the Royal Society, for which we wish to take this opportunity of expressing our thanks.

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CLIX.—*Oxidation of Hydrocarbons of the Benzene Series. Part II. Substances containing a Negative Radicle.*

By HERBERT DRAKE LAW AND FREDERICK MOLLWO PERKIN.

IN continuation of our work on the oxidation of hydrocarbons of the benzene series (Trans., 1907, **91**, 258), we have now studied the action of chromyl dichloride on the nitrotoluenes and the chlorotoluenes, substances which, owing to the presence of a negative group, are difficult to oxidise. With most oxidising agents the methyl group is converted into the carboxyl group, and it is not possible to isolate the alcohol or aldehyde, which should be formed as first products. By means of electrolytic oxidation, Elbs (*Zeitsch. Elektrochem.*, 1896, **2**, 522) has prepared *p*-nitrobenzyl alcohol from *p*-nitrotoluene, whilst Labhardt and Zschoche (*ibid.*, 1902, **8**, 93), by altering the conditions, obtained a mixture of the alcohol and *p*-nitrobenzaldehyde. Pierron (*Bull. Soc. chim.*, 1901, [iii], **25**, 852) also oxidised *o*-nitrotoluene electrolytically, and obtained *o*-nitrobenzaldehyde, but the yield was extremely poor. We have ourselves found it possible to oxidise *o*-nitrotoluene electrolytically, but the yield of the aldehyde is very meagre, never exceeding 4 per cent. of the *o*-nitrotoluene taken. Our method was to suspend the nitrotoluene in a solution of phosphoric acid and sodium phosphate, and by means of a rotating platinum anode to keep it in the form of an emulsion. Owing to the poor yield, however, we did not consider it worth while continuing the work. Étard (*Ann. Chim. Phys.*, 1881, [v], **22**, 218), on oxidising the nitrotoluenes with chromyl dichloride, states that

he obtained nitrotoluquinone. He appears, however, not to have employed the pure nitro-compounds, but the mixture of *o*- and *p*-nitrotoluene obtained by nitrating commercial toluene. The fact that he started with a mixed product would not, of course, affect the formation of the nitrotoluquinone, supposing this to be produced. But as a matter of fact we find that, working with the pure products, nitrotoluquinone is not produced, but that with *p*- and *m*-nitrotoluene good yields of the corresponding aldehydes are obtained. With *o*-nitrotoluene the aldehyde is not formed, but a mixture of chlorinated compounds is produced. Étard gives the melting point of the substance which he identified as nitrotoluquinone as 237° , and describes a number of reactions which he carried out to prove that this substance was a quinone. As a matter of fact, the substance isolated by Étard was *p*-nitrobenzoic acid, which is produced by the oxidation of the aldehyde first formed. The melting point of the acid is 238° , and it is colourless when pure, whereas quinones are always highly coloured. It is rather remarkable that *o*-nitrotoluene, which is such a useful starting point for the preparation of indigo, is so extremely difficult to oxidise to the aldehyde. This difficulty of oxidation is evidently due to the close proximity of the nitro-group to the methyl group.

The chlorotoluenes behave normally, and in each case good yields of the corresponding aldehydes have been obtained.

The action of chromyl dichloride on benzene, naphthalene, anthracene, phenanthrene, fluorene, diphenylmethane, and triphenylmethane has also been studied. The first five substances all react vigorously, but only traces of the quinones were obtained, the bulk of the products consisting of an uninviting substance having no definite melting point, which was insoluble in alkalis and acids and almost insoluble in organic solvents.

Diphenylmethane gave a theoretical yield of benzophenone, and triphenylmethane of triphenylcarbinol.

The action between chromyl dichloride and hydrocarbons of the benzene series containing a negative group is very much slower than with the unsubstituted hydrocarbons. The reaction is accelerated by warming, but generally this was not found advisable, as when this is done there is always a tendency for the reaction to get beyond control.

EXPERIMENTAL.

m-Nitrotoluene.—One hundred grams of *m*-nitrotoluene were mixed with five times its bulk of well-dried carbon tetrachloride, divided into three equal portions, and contained in three flasks of about one litre capacity. The calculated quantity of chromyl dichloride dissolved in twice its volume of carbon tetrachloride was then added to each flask.

The flasks were closed with corks through which tubes containing soda-lime or calcium chloride were passed. The mixtures were now allowed to stand for four weeks, with occasional shaking. At the end of this time, the brown powder which had separated was filtered by the aid of the pump, using an ordinary filter paper, which we find is not attacked by the chromyl dichloride, at any rate when the latter is dissolved in carbon tetrachloride. The product was well washed with carbon tetrachloride until the washings were no longer coloured. The drained product, which, however, still contained a considerable quantity of carbon tetrachloride, was transferred to a beaker and decomposed with a slight excess of a solution of sodium hydrogen sulphite in order to reduce the liberated chromic acid, which would otherwise oxidise a part of the aldehyde. After decomposition, the product was distilled with steam, when a mixture of carbon tetrachloride, unchanged nitrotoluene, and *m*-nitrobenzaldehyde was obtained. Usually sufficient carbon tetrachloride remains in the filtered product to extract all of the other substances from the aqueous distillate, but should this not be the case, an extra quantity is afterwards added. The carbon tetrachloride extract was dried over calcium chloride, and, after distilling off the solvent, the mixture was fractionated. By this means, 50 grams of unchanged nitrotoluene were recovered and 41 grams of aldehyde obtained, that is, 41 per cent. From the residue left after steam distillation, 8 grams of *m*-nitrobenzoic acid were obtained, the melting point of which was 141° .

The aldehyde was identified by its melting point, 58° , and the melting point of its hydrazone, 122° (this is generally given as 121°). A small quantity was also converted into *m*-nitrobenzoic acid, the melting point of which was found to be 141° . The semicarbazones of these aldehydes appear not to have been prepared before. *m*-Nitrobenzaldehyde semicarbazone is pale yellow, and is sparingly soluble in most organic solvents. After crystallisation from a large quantity of glacial acetic acid, it melted and decomposed at 236° . Analysis gave :

N = 27.29, 26.75.

$C_8H_5O_3N_4$ requires N = 26.95 per cent.

p-Nitrotoluene.—Two portions of 50 grams each were dissolved in five times their volumes of carbon tetrachloride and treated with the calculated quantity of chromyl dichloride. After standing, the products were worked up as already described for *m*-nitrotoluene, and 60 grams of the aldehyde (that is, 60 per cent.), also 2 grams of *p*-nitrobenzoic acid, were obtained.

The melting point of the aldehyde was found to be 107° , that of the *p*-nitrobenzoic acid prepared by oxidising the aldehyde, 238° , and the hydrazone melted at 154° . *p*-Nitrotoluene semicarbazone, a pale yellow

substance, after recrystallisation from glacial acetic acid, melted and decomposed at 208° . It is less soluble in acetic acid than the *m*-compound, but more soluble in amyl alcohol. Analysis gave:

N = 27.08.

$C_8H_8O_2N_4$ requires N = 26.95 per cent.

o-Nitrotoluene, treated in a similar manner to the above, yielded a quantity of a brown precipitate, which appeared similar to that produced with *p*- and *m*-nitrotoluenes. On working it up, however, the oil obtained was found not to be the aldehyde, but to consist of chlorinated nitro-compounds of no fixed boiling point, which, on distillation, attacked the eyes severely, so that we have not studied it further.

Chlorotoluenes.

The chlorotoluenes were prepared from the corresponding toluidines by means of Sandmeyer's reaction, and purified by redistillation before use. When the chromyl dichloride is first added to the chlorotoluenes, the reaction is apt to be very vigorous, and on several occasions when the mixture was not kept sufficiently cool by standing the flask containing it in a basin through which cold water was circulated, the reaction took place with explosive violence. At the same time, although the reaction is apt to be vigorous at the commencement, it is as well to leave the products in contact for about two weeks in order to obtain a good yield of the aldehyde.

o-Chlorotoluene.—From 150 grams of the toluene, which were divided into four portions, 66 grams of unchanged substance were recovered and 77 grams of the aldehyde were obtained, that is, 51.5 per cent. The aldehyde was identified by converting it into *o*-chlorobenzoic acid, the melting point of which was found to be 137° .

p-Chlorotoluene.—From 150 grams of the toluene, 46 grams of unchanged substance were recovered and 92 grams of aldehyde were obtained: yield 61.5 per cent. The melting point of the acid prepared from the aldehyde was 239° .

m-Chlorotoluene.—From 110 grams of the toluene, 49 grams of the aldehyde (44.5 per cent.) were obtained. The corresponding acid melted at 153° . As the semicarbazones of these aldehydes do not appear to have previously been described, we have therefore prepared and analysed them.

o-Chlorotoluene semicarbazone separates from pyridine in white, glistening plates, melting at 225 – 226° . Analysis gave:

Cl = 18.01.

$C_8H_7ON_3Cl$ requires Cl = 17.95 per cent.

p-Chlorotoluene semicarbazone crystallises from pyridine in white, glistening plates, melting at 230° . Analysis gave:

Cl = 18.00.

$C_8H_8ON_3Cl$ requires Cl = 17.95 per cent.

m-Chlorotoluene semicarbazone crystallises from pyridine in white, glistening plates, melting at 228°. Analysis gave :

Cl = 17.89.

$C_8H_8ON_3Cl$ requires Cl = 17.95 per cent.

All the semicarbazones are practically insoluble in organic solvents with the exception of pyridine and glacial acetic acid.

Phenanthrene, Anthracene, Naphthalene, and Fluorene.

Black powders were obtained from these hydrocarbons when they were respectively dissolved in carbon tetrachloride and treated with chromyl dichloride. On decomposing the chromyl compounds with water, uninviting products, practically insoluble in all solvents, were produced. Although in the case where anthracene was oxidised there was no difficulty in obtaining the anthranol reaction, we were not successful in isolating the quinones.

Diphenylmethane.

Thirty grams of diphenylmethane were dissolved in 300 c.c. of carbon tetrachloride, placed in a glass vessel surrounded with water, and rather more than the calculated quantity of chromyl dichloride dissolved in 200 c.c. of carbon tetrachloride slowly run in, the mixture being vigorously agitated. When all the chromyl dichloride had been added, the product was allowed to stand overnight. A black mass was obtained, which was collected and washed with carbon tetrachloride by the aid of the pump until the filtrate was colourless. As much as possible of the tetrachloride was removed by pressing. The black cake was then decomposed with water, and the product subjected to steam distillation to remove the remaining carbon tetrachloride. On cooling, benzophenone (m. p. 68°) crystallised out in practically theoretical amount.

Triphenylmethane.

Fifty grams of triphenylmethane were dissolved in 400 c.c. of carbon tetrachloride, and treated with slightly more than the calculated quantity of chromyl dichloride in exactly the same way as diphenylmethane. On working up the black product, an almost theoretical yield of triphenylcarbinol (m. p. 160°) was obtained.

It should be mentioned that most of the chromyl dichloride products are almost black when moist with carbon tetrachloride, chloroform, &c., but if these are expelled at a gentle heat, a very soft, pale brownish-coloured powder is obtained. When decomposing them with water, or,

as was generally done, with sulphurous acid, the solid should only be added in small quantities at a time. If large quantities are added at one time, the particles are inclined to adhere together, and considerable quantities of resinous products are frequently obtained.

The action of chromyl dichloride on hydrocarbons of the aliphatic series is now being investigated.

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CLX.—*The Measurement of a Homogeneous Chemical Change in a Gas. (The Thermal Decomposition of Ozone.)**

By HERBERT EDMUND CLARKE and DAVID LEONARD CHAPMAN.

JUDGING by the published experience of those chemists who have made a special study of chemical changes in gases during recent years, and particularly since Victor Meyer investigated the conditions of the union of hydrogen and oxygen, we should doubtless be compelled to conclude that slow pyrogenic changes in gases have their seat of action principally, if not entirely, on the walls of the enclosing vessels, and that any attempt to measure the velocity of change within a gas itself would be unsuccessful, owing to the impossibility of estimating the precise effect of surface.

A moment's consideration, however, will make it clear that if we could be certain that only a small fraction of the total chemical change were confined to the gas not in the neighbourhood of the walls of the containing vessel, then the effect of surface might be almost entirely eliminated by increasing the size of the vessel until the ratio of its internal surface to its volume became very small. The only difficulty in the way of measuring the velocity of a homogeneous chemical change in the gas would then be the practical one attending the use of a vessel the dimensions of which were large enough for the purpose.

In the present communication, we shall show that, as a matter of fact, the influence of surface on the rate of thermal decomposition

* Compare E. Warburg (*Sitzungsber. K. Akad. Wiss. Berlin*, 1901, 48, 1126), also E. P. Ferman and R. H. Greaves (*Proc. Roy. Soc.*, 1908, A, 80, 353). In neither of the above papers is the special point dealt with in the present communication adequately discussed or investigated, the attention of the authors having been directed towards other objects.

of ozone at 100° in a glass vessel becomes negligible when the vessel is increased in size to quite moderate and convenient proportions. Our results for the rate of decomposition of ozone under these conditions are therefore the first recorded examples of measurements of the velocity of a strictly homogeneous change in the gaseous state.

If a gas of given composition undergoes slow chemical change in a vessel of volume V and area A , the rate of change may be expressed approximately by

$$KV + kA,$$

where K is a constant depending on the composition of the gas, and k is another constant depending both on the composition of the gas and the nature of the surface.

The rate of change per unit volume will be

$$K + \frac{kA}{V},$$

and if the action is accompanied by alteration of pressure, we shall have

$$\frac{\delta p}{\delta \tau} \propto K + \frac{kA}{V},$$

p being the pressure at a time τ .

In our experiments, two vessels, of which the ratios $\frac{A}{V}$ were known to be very different, were filled with the same sample of ozonised oxygen, and heated side by side in a bath of boiling water. The rate of increase of pressure was in all cases about the same in each vessel proving that the term $\frac{kA}{V}$, depending on the nature of the surface, could be neglected, and that the rate of decomposition could be taken as directly proportional to K , a constant the value of which at any given temperature and pressure is determined solely by the composition of the gas.

EXPERIMENTAL.

Oxygen, prepared by heating potassium permanganate, was first passed in a slow stream through aqueous potassium hydroxide, and then dried with concentrated sulphuric acid. The gas was submitted to the action of the silent discharge in a glass ozoniser, all air having been previously swept out of this part of the apparatus by a current of oxygen. To ensure uniformity of composition, the gas issuing from the ozoniser was collected in a large globe over concentrated sulphuric acid, and allowed to stand some time before being used.

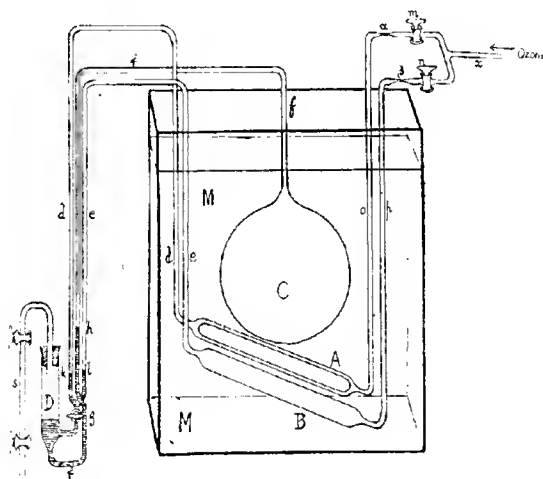
The method adopted for filling the vessels with ozonised oxygen and

for measuring the changes of pressure in each will be understood by reference to Fig. 1.

The bath *M* contains water, which is raised to the boiling point before the filling of the apparatus is started, and maintained at the same temperature while the pressure measurements are being made, the level of the water in the bath being kept constant.

Ozonised oxygen is forced, under pressure, from the globe in which it has been collected into the tube *x*. The gas then divides into two streams, and, passing the opened taps *m* and *n*, reaches the immersed vessels *A* and *B* by the capillary tubes *o* and *p*. The displaced air

FIG. 1.



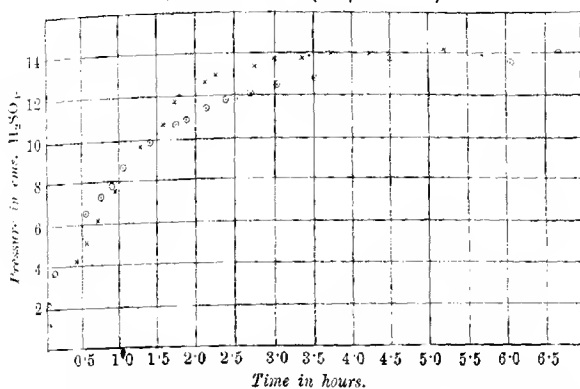
passes along *d* and *e*, and finally escapes through the sulphuric acid contained in the reservoir *D*, the tap *g* being open.

When all the air has been swept out of the apparatus, the capillaries *o* and *p* are sealed off at the constrictions *a* and *β*, and immediately afterwards the pressure of the air above the sulphuric acid in *D* is increased by blowing through the tube *s*, so as to drive sulphuric acid into the manometer capillary tubes *d*, *e*, and *f*. A convenient portion of the scale having been chosen, the positions of the sulphuric acid, *k*, *l*, *h*, in the tubes are carefully recorded.

The capillary tube *f* communicates directly with a large globe, *C*, contained in the bath of boiling water, and, since this tube has a volume very small in comparison with that of the globe, any movement of the sulphuric acid in it cannot appreciably alter the pressure of the

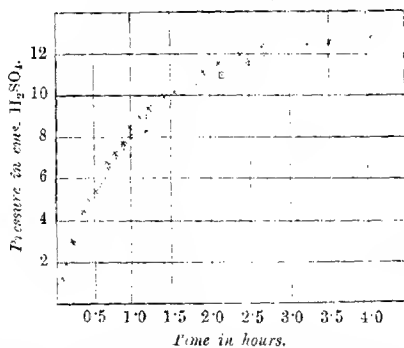
air enclosed in the globe. The perpendicular distance between h and k is therefore a direct measurement, in terms of a column of sulphuric

FIG. 2.
Vessels I and II.—($AV'/AV=2.24$).



acid, of the difference of pressure in C and A . In measuring the variation in this difference of pressure at known intervals during

FIG. 3.
Vessels I and II.—($AV'/AV=2.24$).



The fact that the curves in Figs. 2 and 3 (the records of the results of two successive experiments with the same vessels) are similar, indicates that the rate of decomposition of the ozone is independent of the length of time that the surface of the glass vessels used has been heated in contact with the decomposing gas.

the progress of the decomposition, the sulphuric acid is always brought to the same point, k , so as to keep the volume of gas in A constant.

The readings then furnish a series of numbers from which the rate of increase of pressure in *A* can be deduced.

FIG. 4.
Vessels II and III.—($A'V'/A'V=2.11$).

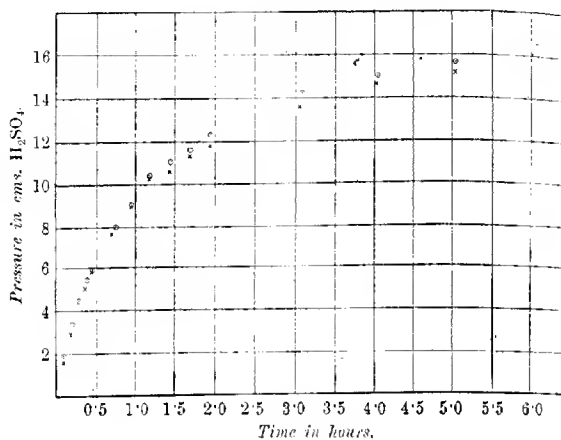
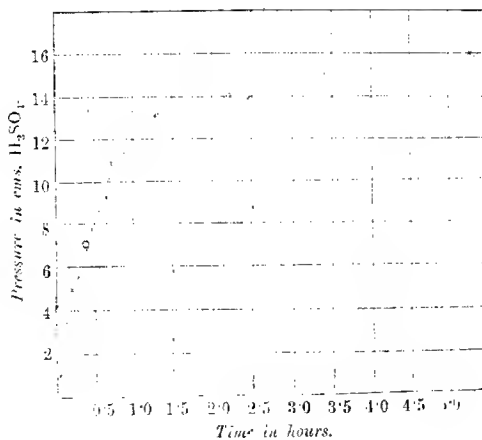


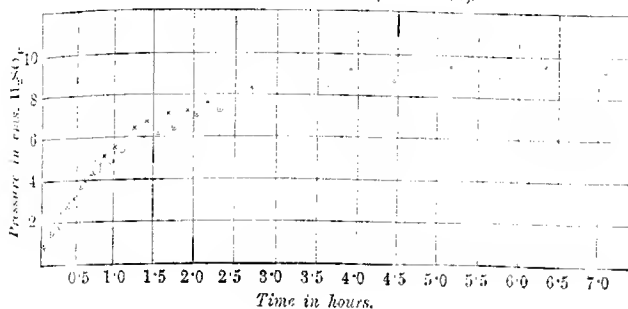
FIG. 5.
Vessels III and IV.—($A'V'/A'V=6.71$).



In the same way the increase of pressure in *B* can be found. The curves obtained by plotting the readings are shown in Figs. 2

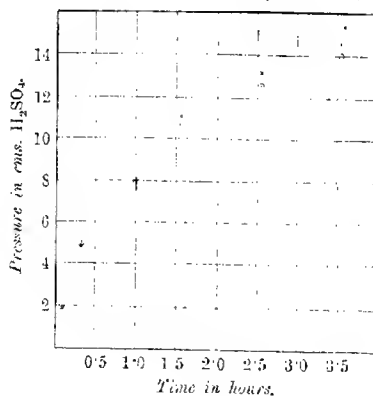
to 8. For convenience in reference, the points corresponding to the increments of pressure in the larger vessel are indicated by circles, and those corresponding to the increments in the other by crosses. The

FIG. 6.
Vessels III and IV.—($AV'/AV=6.71$).



abscissae are the times in hours counting from the first reading, and the ordinates are the increments of pressure in centimetres of sulphuric acid.

FIG. 7.
Vessels II and V.—($AV'/AV=3.92$).



If reference be made to these diagrams, it will be seen that the pressures in both vessels increase at the same rate, although the value of the ratio $\frac{A}{V}$ for one vessel varies in the different experiments

between twice and seven times that of the same ratio for the other.

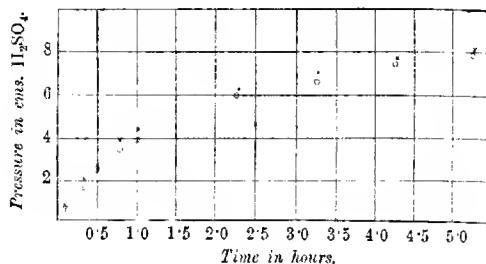
We shall not discuss the question of the order of the reaction until the influence on its rate of gaseous impurities, such as nitrogen and aqueous vapour, has been quantitatively investigated.

Dimensions of Vessels Used.

In the experiments, five different German-glass vessels have been used, the dimensions of which are given in the following tables:

No.	Form.	V , c.c.	A , sq. cms.	A/V , cms ⁻¹ .
I.	Cylinder	138.5	216.8	1.56
II.	"	30.0	104.6	3.49
III.	"	130.5	216.2	1.65
V.	Sphere	161.5	143.4	0.89

FIG. 8.
Vessels II and V.—($AV'/A'V=3.92$).



A and V are the internal surface and volume respectively. Vessel No. IV was a cylinder 28 cms. long, enclosing a shorter concentric cylinder of less radius, closed at both ends, and 26.2 cms. in length. The volume and surface dimensions of this vessel are given below, V_1 and A_1 being respectively the internal volume and area of the outer cylinder, and V_2 and A_2 the external volume and area of the inner cylinder. The ratio of the total surface in contact with the gas to the volume of the gas is therefore given by $\frac{A_1 + A_2}{V_1 - V_2}$.

No.	Form.	V_1 , c.c.	V_2 , c.c.	A_1 , sq. cms.	A_2 , sq. cms.	$\frac{A_1 + A_2}{V_1 - V_2}$, cms ⁻¹ .
IV.	Cylinder within cylinder	128.5	93.5	212.4	175.5	11.68

If in an experiment the ratios of internal surfaces to volumes in the

two vessels be $\frac{A}{V}$ and $\frac{A^1}{V^1}$, the expression $\frac{AV^1}{A^1V}$ gives the number of times the surface per unit volume of the first vessel is greater than that of the second.

With each curve the corresponding value of the ratio $\frac{AV^1}{A^1V}$ is given.

The results demonstrate that under suitable conditions the decomposition of ozone is practically a homogeneous change.

We desire to offer our best thanks to Mr. Underhill, of this College, for his kindly assistance in the later stages of the work.

SIR LEDINE JENKINS LABORATORIES,
JESUS COLLEGE,
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ERRATA.

ERRATA.

DECENNIAL INDEX (1893—1902).

Page	Col.	Line	
1001	ii	5	for "phenyltoluidine" read "phenyltolylamine."
1257	i	24	delete "See also Methylidiphenylamine."

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Page	Line	
1635	1 ²	for "p-Nitrotoluene" read "p-Nitrobenzaldehyde."
1636	6 ²	"o-Chlorotoluene" " "o-Chlorobenzaldehyde."
1636	2 ⁴	"p-Chlorotoluene" " "p-Chlorobenzaldehyde."
1637	3	"m-Chlorotoluene" " "m-Chlorobenzaldehyde."

VOL. XCIV (ABSTR., 1908).

PART I.

468 21 for "ROELKE" read "ROKKER."

PART II.

561 16 for "517" read "644."

719 11*-6² The statement and criticism are wrongly attributed. The statement is by Knoop, the criticism by Friedmann.

From bottom.

two vessels be $\frac{A}{V}$ and $\frac{A^1}{V^1}$, the expression $\frac{AV^1}{A^1V}$ gives the number of times the surface per unit volume of the first vessel is greater than that of the second.

With each curve the corresponding value of the ratio $\frac{AV^1}{A^1V}$ is given.

The results demonstrate that under suitable conditions the decomposition of ozone is practically a homogeneous change.

We desire to offer our best thanks to Mr. Underhill, of this College, for his kindly assistance in the later stages of the work.

SIR LEDGNE JENKINS LABORATORIES,
JESUS COLLEGE,
OXFORD.

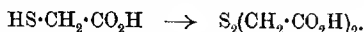
CLXI.—*The Preparation of Disulphides. Part IV.*
Esters of Dithiodiglycollic and Dithiodilactylic
Acids.

By THOMAS SLATER PRICE and DOUGLAS FRANK TWISS.

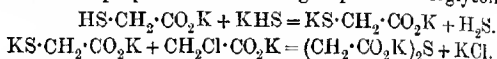
IN our first paper (Trans., 1907, 91, 2021) we have shown that dibenzyl disulphide is readily obtained by submitting sodium benzyl thiosulphate, or the mixture resulting from the interaction of benzyl chloride and sodium thiosulphate in aqueous alcoholic solution, to electrolytic reduction in a divided cell. It has already been shown by other workers (compare Slater, Trans., 1904, 85, 1286; 1905, 87, 482) that the monohalogen substituted derivatives of the fatty acids and esters readily react with sodium thiosulphate, and, on submitting the mixture obtained by the action of sodium thiosulphate on ethyl bromoacetate to electrolysis in the cathode compartment of a divided cell, we found that a heavy oil separated, which proved to be the diethyl ester of dithiodiglycollic acid. The present communication contains an account of the preparation of dimethyl and diethyl dithiodiglycollates, and of the diethyl esters of α -dithio- and β -dithiodilactylic acids. Although the acids corresponding with these esters have been known for some time, the esters, with the exception of diethyl dithiodiglycollate, which was obtained in an impure condition by Claesson (*Ber.*, 1881, 14, 411), do not seem to have been prepared.

The methods which have hitherto been used for the preparation of

these dithio-acids have generally consisted in the oxidation of the corresponding thio-acids (mercaptan acids) by means of iodine or ferric chloride, thus :

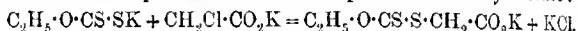


The thio-acids may be prepared from the halogen substituted acids by the action of (a) potassium hydrosulphide, (b) potassium xanthate, and decomposition of the resulting compound by ammonia. The first method is very simple, but unless special precautions are taken it is difficult to obtain a pure product. For example, when potassium chloroacetate is acted on by potassium hydrogen sulphide, not only is thioglycolic acid produced, but also some thiodiglycolic acid, because of the weak acidic properties of the $\cdot\text{SH}$ group in the thioglycolic acid :

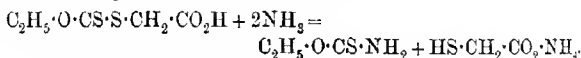


Klason and Carlson (*Ber.*, 1906, 39, 732) have shown, however, that in dilute solution the yield of thioglycolic acid is practically quantitative, since under such conditions the salt, $\text{KS}\cdot\text{CH}_2\cdot\text{CO}_2\text{K}$, cannot exist, being completely hydrolysed to $\text{HS}\cdot\text{CH}_2\cdot\text{CO}_2\text{K}$.

The second method has found extended application in the hands of Holmberg (*J. pr. Chem.*, 1905, [ii], 71, 264; 1907, 75, 169) and Biilmann (*Annalen*, 1905, 339, 351; 1906, 348, 120). To take a particular example, the product of the reaction between potassium chloroacetate and potassium xanthate is potassium xanthylacetate :



The corresponding acid is then dissolved in excess of ammonia, and the solution gently warmed. On cooling, xanthamide crystallises out, and thioglycolic acid may be obtained from the filtrate by the addition of sulphuric acid and extraction with ether :

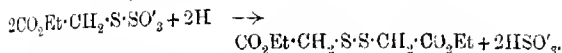
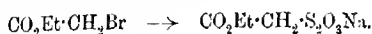


It will be seen from the above that the first method often gives an impure product, and that the second method is somewhat complicated; moreover, the dithio-acid has still to be obtained from the mercaptan acid.

Comparatively recently, Friedländer and Chwala (*Monatsh.*, 1907, 28, 247) have shown that dithiodiglycolic acid may be obtained readily by the direct action of a mixture of sodium sulphide and sulphur, in such proportions as to give the disulphide Na_2S_2 , on sodium chloroacetate.

As already indicated, our method of preparation of the esters of these dithio-acids is as follows, taking diethyl dithiodiglycollate as an example. A mixture of ethyl bromoacetate with a slight excess of sodium thiosulphate in aqueous alcoholic solution is heated on the

water-bath until the pungent odour of the bromoacetate has disappeared. To the cold solution a slight excess of potassium hydrogen carbonate is added, and the mixture transferred to the cathode compartment of a divided cell, the anolyte consisting of a solution of sodium carbonate. A rotating platinum cathode, such as is used in rapid electro-analysis, or similar to the rotating electrode described in F. Mollwo Perkin's *Practical Methods of Electrochemistry*, p. 198, is employed, and the theoretical amount of current passed through the apparatus. Very soon after the current has been started, the catholyte becomes cloudy, owing to separation of the ester. At the end of the electrolysis, the ester is extracted by ether, and the ethereal solution well washed with water and dried; the ether is evaporated, and the residual ester purified by distillation under reduced pressure, one such distillation being sufficient†.



The yield of crude ester generally obtained is from 60 to 70 per cent.; it is not advisable to pass more than the theoretical current, otherwise an appreciable amount of the ester is hydrolysed by the alkaline catholyte, and a decreased yield results. The object of using bicarbonate in preference to carbonate in the cathode liquid is to prevent the formation of free caustic alkali to any extent. The presence of free caustic alkali would be detrimental in two ways: it would hydrolyse some of the ester, and it would further decompose some of the salt resulting from such hydrolysis. It is because of this decomposition that dithio-acids and esters cannot be prepared by the action of caustic alkali on the corresponding thiosulphate derivatives, as is the case with dibenzyl disulphide, &c. (Trans., 1908, 93, 1395, 1401). We have not investigated the decomposition which takes place, further than showing that a thio-acid (mercaptan acid) is produced, which gives the usual colour reactions with ferric chloride, and is oxidised by iodine to the dithio-compound. The reaction is probably similar to that of sodium hydroxide on the anilide of dithiodiglycollic acid (Fericichs and Wildt, *Annalen*, 1908, 360, 105), which is decomposed with the formation of thio-oxanilide, sodium thioglycollate, and thioglycollanilide as primary products.

That these dithio-esters are so readily formed in the manner indicated is further evidence in support of the statement in our first paper (*loc. cit.*) that the formation of disulphide is due to the electrolytic reduction of the complex thiosulphate anion. The fact that dibenzyl disulphide can also be prepared by the action of caustic alkali or alkali carbonate on sodium benzyl thiosulphate (Trans., 1908,

93, 1395) does not show that this is the reaction which really takes place during electrolysis, for the following reasons: (1) The experiments in which the hydrogen evolved during electrolysis was measured (Trans., 1907, 91, 2021) prove that hydrogen is actually used in the reduction. (2) The reaction with alkali is comparatively slow, whereas the electrolytic action takes place rapidly. (3) The electrolytic product is practically pure, and yields of more than 80 per cent. are obtained, whereas with sodium hydroxide a very impure product is formed, and the yield is about 60 per cent.

For complete identification of the esters, the corresponding acids have been prepared by hydrolysis of the esters with hydrochloric acid. As already mentioned, they cannot be obtained by hydrolysis with alcoholic sodium or potassium hydroxide, because of the decomposition which takes place.

EXPERIMENTAL.

Diethyl dithiodiglycollate, $S_2(CH_2 \cdot CO_2 \cdot C_2H_5)_2$.—A mixture of 15 grams of ethyl bromoacetate and 24 grams of sodium thiosulphate with 50 c.c. of water and 50 c.c. of alcohol (80 per cent.) was heated on the water-bath under a reflux condenser for three-quarters of an hour, after which time the pungent odour of the bromoacetate had completely disappeared. After cooling the clear solution so obtained, 75 c.c. more water and 9 grams of potassium hydrogen carbonate* were added (8.98 grams are equivalent to the ethyl bromoacetate taken), and the resulting mixture electrolysed in the cathode compartment of a divided cell (Trans., 1907, 91, 2021), using a rotating cathode; the anolyte was a 10 per cent. solution of sodium carbonate, the anode being a strip of platinum foil. The current which is theoretically necessary is 2.41 ampere-hours, and since it is advisable to use a low current density in order to make the reaction as complete as possible, and at the same time not to allow the process to proceed too long, whereby the ester is decomposed by the alkaline liquid, 0.25 ampere was passed for about three hours and 0.5 ampere for the remainder of the time; the area of the cathode, which was of smooth platinum, was 0.5 sq. dm. In order to keep the bicarbonate in excess, 3 grams more were added when the change of current was made; it was not advisable to add it all at the commencement of the electrolysis, because it would not dissolve completely.

The ester separated as a heavy oil; it was dissolved in ether, the ethereal solution well washed with water and dried; after evaporating off the ether, the remaining liquid was distilled under a pressure of 14 mm., when it practically all passed over at 164°. Diethyl dithiodiglycollate is a fairly mobile liquid, heavier than

* The potassium salt is preferable to the sodium salt because it is more soluble.

water, and possessing a peculiar odour, which is not very disagreeable, and not at all like that which is usually associated with the liquid mercaptans and disulphides. Claesson (*Ber.*, 1881, 14, 411), who had previously prepared this ester from the corresponding acid, describes it as having an unpleasant odour, and boiling at 280° under atmospheric pressure with partial decomposition.

The average yield of crude ester obtained in each experiment was 70 per cent. ; it did not vary much whether the 0.25 ampere was passed for two or for three and a-half hours before raising the current, or whether the current was first put at 0.5 ampere for some time and then reduced to 0.25 ampere. The yield was diminished, however, if the full number of ampere-hours were passed at 0.25 ampere, or if the current was passed for much more than the theoretical time.* During the electrolysis there was a slight odour evolved, which is best described as being similar to that of harm, and which is indicative of decomposition being brought about by the alkaline catholyte. In fact, if some of the ester is heated with alcoholic sodium hydroxide, the same odour is observed, but, owing to it being more pronounced, it becomes very disagreeable and clings most tenaciously to one's clothing.

It is important to wash thoroughly the ethereal solution of the ester; if this is not done, the oil which remains after evaporating off the ether has a disagreeable odour, and on distillation some slight decomposition occurs, which gives the distillate a decided pink colour; the boiling point remains unaffected, however, and distillation of the main fraction, that is, of nearly all the ester, takes place at a constant temperature.

The ethyl ester was also prepared from ethyl chloroacetate. A mixture of 12 grams of the latter, 26 grams of sodium thiosulphate, 50 c.c. of water, and 50 c.c. of alcohol was heated for two and a-half hours over a small flame under reflux, since ethyl chloroacetate reacts much more slowly than the bromoacetate. The remainder of the operation was similar to that already described with ethyl bromoacetate. Ten grams of potassium hydrogen carbonate (theoretical quantity = 9.8 grams) and 50 c.c. more water were added at the commencement of the electrolysis, which was continued for 2.63 ampere-hours, 0.25 ampere being passed for about two hours and 0.5 ampere for the remainder of the time; four grams more of bicarbonate were added when the current was changed. The average yield of ester was 70 per cent. :

0.2923 gave 0.5718 BaSO_4 . $S = 26.86$.

$\text{C}_8\text{H}_{14}\text{O}_4\text{S}_2$ requires $S = 26.92$ per cent.

* The same remarks with respect to yield apply also to the other esters prepared. The area of the cathode was, in each case, 0.5 sq. dm.

Dimethyl dithiodiglycollate, $S_2(CH_2 \cdot CO_2 \cdot CH_3)_2$, was prepared and purified in a similar manner to the diethyl ester. A mixture of 15 grams of methyl bromoacetate, 26 grams of sodium thiosulphate, 50 c.c. of water, and 50 c.c. of alcohol was heated for three-quarters of an hour on the water-bath. For the electrolysis, 10 grams (theoretical quantity = 9.8 grams) of potassium hydrogen carbonate and 50 c.c. more water were added, and the current passed for 2.63 ampere-hours, using 0.25 ampere for three hours and 0.5 ampere for the remainder of the time; 3 grams more bicarbonate were added during the electrolysis. The average yield of crude ester obtained was 60 per cent., which is somewhat less than that of the diethyl ester, the latter not being so readily attacked by the alkaline catholyte as the former. During the electrolysis the harm-like odour becomes very pronounced.

It is especially necessary to wash the ethereal solution of this ester thoroughly, otherwise, on distillation, the distillate begins to show a pink colour almost immediately, finally becoming a rich ruby-red. Even when the ethereal solution has been well washed, the last portions of the distillate are liable to be coloured pink.

Dimethyl dithiodiglycollate is a fairly mobile liquid, heavier than water, and possessing an odour similar to that of the diethyl ester. It distils at 154° under a pressure of 14 mm.:

0.2294 gave 0.5047 $BaSO_4$. $S = 30.21$.

$C_4H_{10}O_4S_2$ requires $S = 30.50$ per cent.

Dithiodiglycollic acid, $S_2(CH_2 \cdot CO_2H)_2$, was prepared by heating the diethyl ester with hydrochloric acid under a reflux condenser until a homogeneous solution resulted, and then extracting the solution with ether. The residue from the dried ethereal extract was recrystallised from a mixture of one part of ethyl acetate and nine parts of benzene; the crystals so obtained melted at $107-108^\circ$ (compare Billman, *Annalen*, 1905, 339, 351; Holmberg, *Zeitsch. anorg. Chem.*, 1907, 56, 385, who also give references to the earlier literature):

0.1991 required 16.00 c.c. of 0.1366 $N/1$ $NaOH$ for complete neutralisation. Equivalent = 91.10.

$C_4H_6O_4S_2$ requires equivalent = 91.08

Diethyl α -dithiodilactylate, $S_2(CHMe \cdot CO_2 \cdot C_2H_5)_2$, was prepared from ethyl α -bromopropionate. The reaction mixture consisted of 16 grams of ethyl α -bromopropionate, 23 grams of sodium thio-sulphate, 50 c.c. of alcohol, and 50 c.c. of water, and was heated for three-quarters of an hour on the water-bath. For the electrolysis, 9 grams of potassium hydrogen carbonate (theoretical quantity = 8.84) and 75 c.c. more water were added, and the current passed for 2.37 ampere-hours, using 0.25 ampere for three and a-half hours, and 0.5 ampere for the

remainder of the time; 3 grams more bicarbonate were added at the end of three and a-half hours. There was very little odour noticeable during the electrolysis. The ester separated as a heavy oil; it was treated in the way already described, although in this case it was not so necessary to wash the ethereal solution with water.

Diethyl α-dithiodilactylate is a fairly mobile liquid, heavier than water, and possessing a peculiar odour similar to that of diethyl dithiodiglycolate. It distils at 159° under a pressure of 14 mm.:

0.2442 gave 0.4268 BaSO₄. S = 24.00.

0.2105 „ 0.3713 BaSO₄. S = 24.22.

C₁₀H₁₈O₄S₂ requires S = 24.08 per cent.

α-Dithiodilactylic acid, S₂(CHMe·CO₂H)₂, was prepared by heating the ester with hydrochloric acid until it had disappeared. The hydrolysis took place very slowly. The solution so obtained was evaporated to dryness on the water-bath and the residue recrystallised several times from water, in which the acid is fairly soluble: .

0.1941 gave 0.4282 BaSO₄. S = 30.30.

0.1948 required 13.60 c.c. of 0.1366 N/1 NaOH. Equivalent = 104.9.

0.1976 „ 13.78 c.c. „ 0.1366 N/1 NaOH. „ = 105.0.

C₈H₁₀O₄S₂ requires S = 30.50 per cent., and equivalent = 105.1.

Although the above figures show that the acid was pure, it did not melt sharply; it showed signs of softening at about 117°, and, as the temperature was raised, the crystals clotted together, until at about 139° they began to melt, forming a clear liquid in which crystals of the acid remained suspended. The last particle of solid did not disappear until 142°. No matter how often the acid was recrystallised, the same phenomena were observed. An examination of the literature shows that previous investigators (Mörner, *Zeitsch. physiol. Chem.*, 1904, 42, 353; Büllmann, *Annalen*, 1905, 339, 351) have obtained similar results, but no explanation has been given. The quantity of acid at our disposal at present is too small for us to investigate the matter fully, but we are preparing further quantities with that end in view.* We have found, however, that, on keeping, the acid at a temperature of 150–160° for several hours, the equivalent remained unaltered (105.3 instead of 105.1), but the melting point changed; the substance then began to soften at 110°, partly melted at 119°, and the last particle of solid disappeared at 127°.

Diethyl β-dithiodilactylate, S₂(CH₂·CH₂·CO₂·C₂H₅)₂, was prepared from ethyl β-iodopropionate, the method of procedure being exactly the

* Soon after this paper had been submitted to the Chemical Society, an abstract appeared of a paper by Lovén (*J. pr. Chem.*, 1908, [ii], 78, 63) on "Optically Active Thiolactic and Dithiodilactylic Acids." He shows that α-dithiodilactylic acid, as ordinarily prepared, is a mixture of the racemic and meso-forms; hence the anomalous behaviour mentioned in the text.

same as for the α -ester. The quantities of reagents taken were 14.2 grams of ethyl β -iodopropionate, 17 grams of sodium thiosulphate, 50 c.c. of water, and 50 c.c. of alcohol. Seven grams of potassium hydrogen carbonate and 50 c.c. of water were added for the electrolysis, and the current was passed for 1.67 ampere-hours, using 0.25 ampere for three hours and 0.5 ampere for the remainder of the time. Two grams of bicarbonate were added when the current was increased. When the mixture was being heated on the water-bath, and also for a short time at the commencement of the electrolysis, there was a strong garlic odour. The ester separated as an oil, and was treated in the same way as the α -ester.

Diethyl β -dithiodilactylate has similar physical properties to the isomeric α -ester. It distils at 194° under a pressure of 17 mm.:

0.2247 gave 0.3930 BaSO_4 . $S = 24.02$.

0.2182 „ 0.2836 BaSO_4 . $S = 24.14$.

$\text{C}_{10}\text{H}_{18}\text{O}_4\text{S}_2$ requires $S = 24.08$ per cent.

β -Dithiodilactylic acid, $\text{S}_2(\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$, was prepared from the ester by hydrolysis with hydrochloric acid, as in the case of the α -acid. Hydrolysis took place much more rapidly than with the α -ester, and, on cooling, the acid crystallised out. It was recrystallised several times from water, and then melted at 155° , although it showed signs of softening at a temperature some degrees lower. The melting point and other properties agreed with those previously observed (compare Biilmann, *Annalen*, 1905, 339, 351):

0.1971 required 13.65 c.c. of 0.1366 $N/1$ NaOH . Equivalent = 105.7.

$\text{C}_6\text{H}_{10}\text{O}_4\text{S}_2$ requires equivalent = 105.1 per cent.

We hope to give an account of the physical properties of the esters described in this paper, and also of homologous esters, in the near future.

Part of the expense of the foregoing investigation was defrayed by a grant awarded by the Committee of the Research Fund, for which we wish to express our thanks.

Addendum.—Since the publication of Part II (*Trans.*, 1908, 93, 1395), we have found that Bernthsen has prepared a number of organic thiosulphate derivatives, which, unlike those we have so far studied, contain the sulphur atom directly attached to the benzene nucleus; he has also shown that the corresponding disulphide is produced by the action of sodium hydroxide (*Annalen*, 1889, 251, 1). For example, *p*-aminodimethylaniline thiosulphuric acid, $\text{NMe}_2\cdot\text{C}_6\text{H}_3(\text{NH}_2)\cdot\text{S}\cdot\text{SO}_3\text{H}$, was prepared from *p*-aminodimethylaniline and sodium thiosulphate by oxidation with potassium dichromate in the presence of aluminium

sulphate. On warming with dilute sodium hydroxide, the impure disulphide was produced. A preliminary experiment which we have made shows that the disulphide is also readily produced by electrolysis, and it is apparently uncontaminated by mercaptan, whereas Bernthsen states that the isolation of the disulphide in a fairly pure state is a matter of great difficulty.

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CLXII.—*The Constituents of the Expressed Oil of Nutmeg.*

By FREDERICK BELDING POWER and ARTHUR HENRY SALWAY.

HAVING undertaken a complete study of the constituents of the nutmeg, the essential oil of which has already been investigated by us (*Trans.*, 1907, **91**, 2037), it was necessary to obtain somewhat more precise information than is at present available respecting the composition of the expressed oil or fat. An examination of the latter appeared the more important in view of the fact that the nutmeg is known to possess narcotic properties, and that the only known constituent to which it has been possible to attribute this action is myristicin, $C_{11}H_{12}O_3$ (3-methoxy-4:5-methylenedioxy-1-allylbenzene), which is a component of the essential oil, and therefore also contained in the expressed oil or fat.

The deficiency of knowledge respecting the constituents of the expressed oil of nutmeg, commonly known as "nutmeg butter," is indicated by the following statement recorded in Lewkowitsch's *Chemical Technology and Analysis of Oils, Fats, and Waxes*, Vol. II., p. 718: "This fat varies considerably in its composition. It contains from 4 to 10 per cent. of an ethereal oil, and consists of about 45 per cent. of a solid fat—chiefly trimyristin—the rest being a liquid fat and free fatty acids." The only further information of importance regarding the composition of this fat appears to be the statement that the liquid portion consists chiefly of olein (compare Koller, *Arch. Pharm.*, 1865, **173**, 286; Benedikt, *Analyse der Fette und Wacharten*, 4te Aufl., 1903, p. 572; C. R. Alder Wright, *Fats and Oils*, 2nd ed., 1903, p. 546; Hefter, *Technologie der Fette und Oele*, 1907, Bd. II., p. 627). Although a genuine expressed oil of nutmeg is likely to vary considerably in character, it is quite probable that the statements recorded concerning its composition are based, for the most part, on the examination of commercial products, which are often of uncertain origin and subject to adulteration.

EXPERIMENTAL.

For the purpose of a complete examination of the constituents of nutmeg fat, a quantity of it was kindly expressed for us by Messrs. Stafford Allen and Sons, of London, the material employed having been a portion of the same lot of Ceylon nutmegs as that from which the essential oil previously examined had been distilled (Trans., 1907, 91, 2037).

The crushed nutmegs (23·7 kilograms), after being warmed, were subjected to a pressure of 4000 pounds per square inch, at a temperature ranging between 45° and 75°, for a period of eight hours, and were then allowed to remain under pressure at a gradually decreasing temperature for about twelve hours. The total amount of fat thus obtained was 6·3 kilograms, corresponding to a yield of 26·6 per cent. This fat, at the ordinary temperature, was a soft, brownish-yellow solid, possessing the characteristic odour of nutmeg. A portion of the same lot of nutmegs, when finely ground and extracted in a Soxhlet apparatus with ether, yielded 42·9 per cent. of fat.

The total amount of expressed fat was liquefied by a gentle heat, and subsequently stirred until it solidified, in order to render it perfectly homogeneous. Determinations were then made of the constituents of the expressed fat, of that obtained by extraction with ether, and of the expressed fat from which the essential oil had been removed, as also of the total fatty acids. The results were as follows:

	Expressed fat.	Fat extracted by ether.	Expressed fat free from essential oil.	Total fatty acids.
Melting point	48°	50°	46°	48°
Density 50°/50°	0·9399	0·9337	0·9443	0·9012
Acid value.....	11·2	12·0	14·0	218·3
Saponification value..	174·6	180·5	199·6	—
Iodine value.....	57·8	45·7	35·7	23·1

An observation by Lewkowitsch (*loc. cit.*, p. 719), that the iodine value of nutmeg fat is not appreciably altered by the removal of the essential oil, cannot be confirmed by the above figures.

Separation of the Essential Oil and Tringristin.

A quantity (2000 grams) of the expressed fat was heated in a current of steam until the essential oil had been removed as completely as possible. The aqueous distillate, which contained a quantity of oil, had a faintly acid reaction. It was extracted twice with ether, the ethereal liquid being washed with a little water, dried with anhydrous sodium sulphate, and the ether removed. About 250 grams of

essential oil were obtained, thus representing 12.5 per cent. of the weight of nutmeg fat employed. The essential oil had the following characters: D_4^{20} 0.8794; n_D^{20} + 22°30' in a 1-dm. tube.

The aqueous distillate, which had been extracted with ether, still contained a very small amount of volatile acid, which, after conversion into a barium salt, was found to consist chiefly of a mixture of formic and acetic acids.

The contents of the distillation flask, after being allowed to cool, consisted of a solid cake of fat, together with some water. The fat was removed and dissolved in hot alcohol, when, on cooling, a large amount of a crystalline solid separated. This was purified by several crystallisations from hot alcohol, after which it was quite colourless, and melted at 54—55°.

0.1453 gave 0.3962 CO_2 and 0.1588 H_2O . $\text{C} = 74.4$; $\text{H} = 12.1$.

$\text{C}_3\text{H}_5(\text{C}_{14}\text{H}_{27}\text{O}_2)_3$ requires $\text{C} = 74.8$; $\text{H} = 11.9$ per cent.

This substance was thus identified as trimyristin.

Hydrolysis of the Fatty Oil.

The alcoholic mother liquors from the trimyristin were united and heated for an hour on a water-bath with an excess of potassium hydroxide. The greater part of the alcohol was then removed, water added, and the alkaline mixture repeatedly extracted with ether.

Unsaponifiable Constituents of the Oil.

The ethereal liquids, obtained by the extraction of the above-mentioned alkaline mixture, were combined, washed, dried, and the ether removed, when a quantity (170 grams) of a thick, yellow liquid was obtained. On dissolving this in warm 70 per cent. alcohol, and allowing the solution to stand, a small amount of solid was deposited, which was removed, and subsequently crystallised from a mixture of ethyl acetate and alcohol. It was thus obtained in colourless, glistening leaflets, melting at 134—135°:

0.1679, when dried at 105°, lost 0.0094 H_2O . $\text{H}_2\text{O} = 5.6$.

0.1090 gave 0.3304 CO_2 and 0.1180 H_2O . $\text{C} = 82.7$; $\text{H} = 12.0$.

$\text{C}_{20}\text{H}_{34}\text{O}, \text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 5.8$ per cent.

$\text{C}_{20}\text{H}_{34}\text{O}$ requires $\text{C} = 82.8$; $\text{H} = 11.7$ per cent.

The composition of this substance, together with its characteristic colour reactions, established its identity as a phytosterol.

Isolation of a New Substance, $\text{C}_{18}\text{H}_{32}\text{O}_2$.

The alcoholic solution of unsaponifiable material, from which the phytosterol had been separated as above described, was freed from

alcohol, and the residual product fractionally distilled under 15 mm. pressuro. After several distillations, the following fractions were collected: 140—170° (27 grams); 170—200° (25 grams); 200—260° (5 grams); 260—270° (16 grams); 270—280° (55 grams).

The lowest boiling fraction was a limpid liquid, and contained a considerable proportion of myristicin, which was identified by means of its bromo-derivative (m. p. 128—129°). The fraction boiling at 270—280°/15 mm. was the largest in amount, and possessed the most constant boiling point. At the ordinary temperature, it was a yellow, transparent, extremely viscid liquid, which showed no tendency to crystallise, even on long standing. Two different preparations of this substance were analysed, with the following results:

I.	0.2523	gavo	0.6274	CO ₂	and	0.1546	H ₂ O.	C = 67.8; H = 6.8.
	0.1145	„	0.2854	CO ₂	„	0.0732	H ₂ O.	C = 68.0; H = 7.1.
	0.1380	„	0.3452	CO ₂	„	0.0902	H ₂ O.	C = 68.2; H = 7.3.
II.	0.1902	„	0.4736	CO ₂	„	0.1173	H ₂ O.	C = 67.9; H = 6.9.
	0.2006	„	0.5015	CO ₂	„	0.1258	H ₂ O.	C = 68.2; H = 7.0.
								Mean C = 68.0; H = 7.0.

C₁₁H₁₄O₈ requires C = 68.0; H = 7.2 per cent. M.W. = 194.

C₁₅H₂₂O₅ „ C = 67.9; H = 6.9 „ M.W. = 318.

C₂₆H₃₂O₇ „ C = 68.4; H = 7.0 „ M.W. = 456.

The molecular weight of the substance was determined by the cryoscopic method in benzene solution:

0.1889 in 21.73 of benzene gave $\Delta t = 0.150^\circ$. M.W. = 290.

0.4205 „ 21.73 „ „ $\Delta t = 0.337^\circ$. M.W. = 287.

From a consideration of these results, it would appear probable that the substance possesses the formula C₁₅H₂₂O₅, and this conclusion is supported by a determination of its iodine value:

0.2233 absorbed 0.1707 iodine. I = 76.4.

C₁₅H₂₂O₅, with one ethylenic linking, requires I = 79.9 per cent.

As the above-described constituent of nutmeg fat is quite dissimilar in character to any substance of the formula C₁₅H₂₂O₅ which has hitherto been recorded, it may be regarded as a new compound.

The substance, C₁₅H₂₂O₅, is very readily soluble in all the usual organic solvents, except light petroleum, which dissolves it but sparingly, and it is also soluble in 70 per cent. alcohol. It contains neither hydroxyl nor carbonyl groups, since acetic anhydride, hydroxylamine, and semicarbazide have no action on it. The substance contains, however, at least two methoxyl groups, but an accurate quantitative determination of the latter was not possible owing to the continued slow evolution of alkyl iodide, even after several hours' heating with hydriodic acid. This behaviour is probably to be attributed to a dioxymethylene group which is only slowly attacked by

hydriodic acid. Attempts were made to prepare a crystalline derivative of the substance by acting on it in the cold with bromine and nitric acid respectively, but only amorphous products were obtained. When oxidised with alkaline permanganate, it yielded only uncrystallisable substances of a resinous nature.

As it was thought possible that the above-described substance, $C_{15}H_{32}O_5$, might possess some definite physiological action, it was kindly tested for us by Dr. H. H. Dale, Director of the Wellcome Physiological Research Laboratories. It was ascertained, however, that when administered to cats, in doses of 0.5 and 1 gram respectively, no obvious effects were produced.

The Fatty Acids.

The alkaline, aqueous solution of potassium salts, resulting from the above-described hydrolysis of the fatty oil, was acidified with sulphuric acid and distilled with steam. No acid was found in the distillate with the exception of a very small quantity of myristic acid. The fatty acids remaining in the distillation flask were then extracted with ether, when a quantity (about 30 grams) of an insoluble, black resin separated. This was collected and extracted with various solvents, but nothing crystalline could be obtained from it.

The above-mentioned ethereal solution was subsequently washed, dried, and the ether removed, when the fatty acids were obtained in the form of a solid cake. These acids, when dissolved in chloroform, were devoid of optical activity. They were distilled under diminished pressure, and the following fractions collected: 205—220°; 220—245°; above 245°/20 mm.; a small amount of undistillable resin remaining in the flask.

Fraction 205—220°/20 mm.—This formed a solid mass, and amounted to 310 grams. After crystallisation from alcohol, a product was obtained, which melted at 53—54°, and was found to consist of myristic acid:

0.1125 gave 0.3027 CO_2 and 0.1257 H_2O . $C = 73.4$; $H = 12.4$.

$C_{14}H_{28}O_2$ requires $C = 73.7$; $H = 12.3$ per cent.

Fraction 220—245°/20 mm.—This fraction amounted to about 100 grams, and became partly solid on cooling. The solid portion was separated by filtration, and, after crystallisation from alcohol, was identified as myristic acid. The liquid portion of this fraction, together with the alcoholic mother liquors from the preceding one, was neutralised with potassium hydroxide, and treated with an alcoholic solution of lead acetate. The precipitated lead salt was washed with water, digested with ether, and the filtered ethereal liquid shaken with dilute hydrochloric acid. The ethereal liquid was then separated from

the lead chloride, washed with water, dried, and the ether removed, when about 50 grams of unsaturated acids were obtained. On distilling this product, it was found that the greater portion boiled between 220° and 230° under a pressure of 10 mm. :

0.2030 gave 0.5633 CO_2 and 0.2039 H_2O . $\text{C} = 75.7$; $\text{H} = 11.2$.

0.2246 absorbed 0.2674 iodine. Iodine value = 119.1.

0.3059 neutralised 9.3 c.c. $N/10$ KOH. Neutralisation value = 170.5.

$\text{C}_{18}\text{H}_{34}\text{O}_2$ requires $\text{C} = 76.6$; $\text{H} = 12.1$ per cent. Iodine value = 90.1 ;
Neutralisation value = 199.

The analysis and constants of this product indicated it to be a mixture containing some acid of a higher degree of unsaturation than oleic acid. In order to ascertain more definitely the character of its constituents, a portion (11 grams) was oxidised in alkaline solution with 1000 c.c. of a 1 per cent. solution of potassium permanganate in the cold. The pure white oxidation product was collected and digested with much ether, which extracted a considerable amount of a crystalline solid. This was recrystallised from alcohol, when it was obtained in glistening laminae, melting at $128-129^{\circ}$:

0.1218 gave 0.3041 CO_2 and 0.1298 H_2O . $\text{C} = 68.1$; $\text{H} = 11.3$.

0.0999 „ 0.2497 CO_2 „ 0.1044 H_2O . $\text{C} = 68.2$; $\text{H} = 11.6$.

$\text{C}_{18}\text{H}_{30}\text{O}_4$ requires $\text{C} = 68.4$; $\text{H} = 11.4$ per cent.

This substance was evidently dihydroxystearic acid, and its formation proved the presence of oleic acid in the original mixture.

In addition to the above-mentioned product of oxidation, a very small quantity of a crystalline acid was isolated, which melted at $200-205^{\circ}$. This was doubtless linolic acid (a hexahydroxystearic acid), which is stated to melt at 203° , and its formation indicated the presence of linolenic acid in the oil. As no sativic acid (tetrahydroxystearic acid) could be isolated from the product of oxidation, it may be concluded that linolic acid is not a constituent of the oil, and that the unsaturated acids of nutmeg fat therefore consist chiefly of oleic acid with a small amount of linolenic acid. The presence of the latter is, furthermore, confirmed by the iodine value of the original mixture of liquid acids.

Fraction above $245^{\circ}/20$ mm.—This fraction was small in amount, and consisted of a thick, glutinous, brown oil. On treating it with cold alcohol, it partly solidified. The solid substance was collected and crystallised several times from ethyl acetate, when it appeared quite homogeneous and melted at $74-75^{\circ}$:

0.0599 gave 0.1717 CO_2 and 0.0712 H_2O . $\text{C} = 78.2$; $\text{H} = 13.2$.

$\text{C}_{26}\text{H}_{42}\text{O}_2$ requires $\text{C} = 78.8$; $\text{H} = 13.0$ per cent.

0.1145 neutralised 2.8 c.c. *N*/10 KOH. Neutralisation value = 137.

$C_{26}H_{52}O_2$ requires a neutralisation value of 142.

This substance was undoubtedly cerotic acid.

Summary.

The preceding investigation of a genuine expressed oil of nutmeg has shown its composition to be approximately as follows :

Essential oil	12.5 per cent.
Trimyristin	73.0 "
Oleic acid, as glyceride	3.0 "
Linolenic acid, as glyceride.....	0.5 "
Formic, acetic, and cerotic acids	(very small amounts)
Unsapouifiable constituents ..	8.5 per cent.
Resinous material	2.0 "
	<hr/> 98.5 per cent.

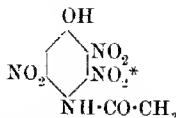
The unsapouifiable constituents consisted of a new compound, $C_{13}H_{22}O_5$ (amounting to about 5 per cent. of the expressed oil), together with some myristicin, $C_{11}H_{18}O_3$, and a very small amount of a phytosterol, $C_{29}H_{54}O$ (m. p. 134—135°). Although the myristicin is a constituent of the essential oil, it was not practicable to effect its complete removal by the preliminary treatment of the fat with steam.

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CLXIII. —*Syntheses with Phenol Derivatives containing a Mobile Nitro-group. Part I. The Interaction of 2:3:5-Trinitro-4-acetylaminophenol and Amines.*

By RAPHAEL MELDOLA, F.R.S., and JAMES GORDON HAY.

THE trinitroacetylaminophenol described by one of us in 1906 (*Trans.*, **89**, 1935) was shown to possess the constitution expressed by the formula :

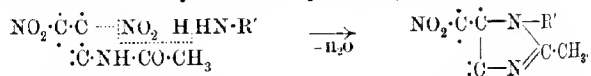


The 3-nitro-group in this compound (marked *) is the mobile radicle, as is proved by the readiness with which derivatives of benzimidazole are formed by the interaction of the trinitro-com-

pound and primary amines. Taking advantage of this property, the investigation has been extended with a view to throwing further light on the mechanism of catenation* and iminazole ring formation. The first question that naturally arose at the outset of the work was whether the extreme mobility of the nitro-group is determined by the presence of the acetyl-amino-group in the ortho-position with respect to the amine residuc which enters the nucleus in place of the 3-nitro-group. This crucial point was studied, in the first place, by investigating the reactivity of the trinitro-compound towards secondary amines, such as dimethyl-amine. It has been found that with such secondary amines condensation quite readily takes place with the formation of derivatives of the corresponding dialkylanilines. Since in these cases no iminazole formation is possible, it is concluded that the tendency to "anhydridise," caused by the presence of the ortho-acetyl-amino-group, has no direct influence on the mobility of the 3-nitro-group. Whether any action at all is exerted by the radicle represented in the present series of iminazoles by the 2-methyl group could be determined by comparing the rate of formation of iminazoles from the same set of amines with acyl derivatives of trinitro-aminophenol containing other radicles in the place of acetyl. The isolation of the 2:3:5-trinitro-4-aminophenol described by us in a recent paper (*Trans.*, 1907, **91**, 1477) should enable the necessary comparison to be made, provided that a satisfactory method can be devised for following the course of the reaction quantitatively. We hope to be able to extend the research in this direction.

The Mechanism of Formation of Iminazoles.

The production of an iminazole by the interaction of trinitro-acetylaminophenol and a primary amine is obviously the result of two processes; first, ordinary catenation between the phenolic and aminic residues after the removal of the nitro-group; and, secondly, the anhydridisation resulting from the interaction of the ortho-substituents. The synthesis is expressed by the scheme:



The intermediate compound is thus a derivative of a substituted diphenylamine or analogous secondary arylamine, a view which is supported by the evidence adduced in the former paper, that, in certain cases, the intermediate secondary amine is sufficiently stable

* This term is proposed as a convenient expression for "chain formation" (*Verkettung*).—R. M.

to be capable of isolation, and can then be converted into the iminazole by dehydration (Trans., 1906, 89, 1940, 1941). From this point of view the action of amines on the trinitro-compound at the ordinary temperature acquires special importance, and systematic experiments will be undertaken in connexion with this part of the subject. That interaction occurs under these conditions is shown by the following experiment, in which aniline was used as the amine.

Four grams of the trinitro-compound were dissolved in 60 c.c. of alcohol, and to this solution aniline in the proportion of three molecules to one of the trinitro-compound was added. The solution, which becomes pulpy at first owing to the separation of the orange crystals of the aniline salt, was kept cooled in a vessel of water, and the contents of the flask were briskly agitated from time to time. In about four and a-half hours the crystals of the aniline salt had disappeared, and the clear solution was then acidified with hydrochloric acid, diluted with water, and the precipitate collected and washed. In order to separate the dinitrohydroxydiphenylamine and iminazole from the other products of the reaction, the washed precipitate was extracted with cold dilute sodium hydroxide, filtered, and the phenolic compounds recovered from the alkaline filtrate by precipitation with acid. The product thus obtained proved to be a mixture having, after crystallisation from alcohol, a melting point ranging from about 160° to 167° . Attempts to separate this mixture by crystallisation or by extraction with cold solvents were unsuccessful. By crystallisation from alcohol, the phenyliminazole (m. p. 188°) was finally isolated, but until some satisfactory method has been devised for determining the actual composition of the mixture it is impossible to state how much of the iminazole is present in the original product, and how much results from anhydridisation during the process of crystallisation. That the product of the interaction of aniline and the trinitro-compound in alcoholic solution at the ordinary temperature is a mixture is shown by microscopic examination, which reveals the presence of two kinds of crystals, and also by analysis, the following result having been obtained from a crop of crystals deposited from alcohol after the first crop of crystals of the iminazole had been removed:

0.0815 gave 12 c.c. N_2 (moist) at 18° and 769.8 mm. $N = 17.24$.

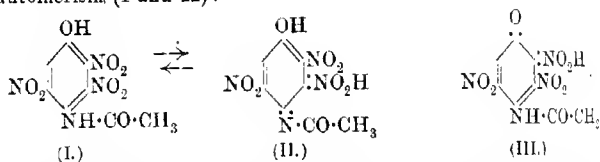
The diphenylamine derivative, $C_{14}H_{12}O_6N_4$, requires $N = 16.88$; the iminazole, $C_{14}H_{10}O_5N_4$, requires $N = 17.87$ per cent. A mixture in equimolecular proportions of the two compounds requires $N = 17.38$ per cent. The mixed product is converted into the iminazole by the action of heat; after determining the melting

point, the compound solidified, and then fused again at 186°. Anhydridisation is best effected by boiling a solution of the sodium salt for about fifteen minutes. If excess of sodium hydroxide is present, large, orange crystals of the sodium salt of the iminazole separate out as the solution cools.

The nitro-group in all these decompositions is eliminated in the form of nitrous acid, and the secondary products are accordingly such as might be expected to arise from the action of this acid on the free amine present in the solution.

The Mobility of the Nitro-group in Relation to the Constitution of the Trinitro-compound.

The extreme mobility of the 3-nitro-group, which is well shown by the foregoing experiment, suggests that this group is attached to the nucleus in some different way from the other groups. We prefer for the present to indicate this property by a dotted line showing the "bond," as in the foregoing scheme. There is, however, another mode of representation, which, in view of recent developments in the theory of the constitution of nitro-compounds, appears worthy of consideration, although we are at present unable to adduce any direct evidence in its support. The mobile nitro-group, being adjacent to the acetyl-amino-group, admits of "isonitro" tautomerism. (I and II):



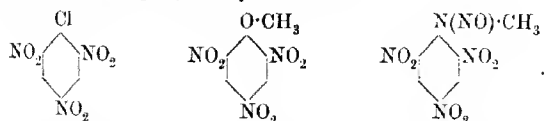
Some support is given to this view by the fact that trinitro-acetylaminophenol in the solid condition is pale yellow, whilst its aqueous solution is orange and its salts are a deep orange-red. But any conclusion concerning the mode of attachment of the mobile nitro-group, based on evidence furnished by colour, is weakened by the circumstance that the 2-nitro-group is also susceptible of "isonitro" formulation, as shown above (III). Formula II also has the disadvantage of necessitating a complicated series of additions and rearrangements in order to explain the formation of the secondary amine derivative, which is undoubtedly in all cases the first product of the reaction.

The reactivity of the trinitro-compound may be most rationally regarded as an extreme case of the mobility of a negative radicle contained in a nucleus already highly charged with such radicles.

the positions of the 2-nitro- and the acetylamino-group being specially favourable in this case for exerting a loosening influence on the mobile group. Many compounds of this type are known to chemists, although the present case is perhaps extreme so far as it concerns the mobility of a nitro-group. Among recently-discovered compounds which owe their activity to a mobile radicle, and which therefore present an analogy to trinitroacetylaminophenol, we may refer to the dichloro- and dibromo-dinitrobenzenes studied by Blanksma (*Rec. trav. chim.*, 1908, 27, 42), in which one of the nitro-groups is also replaceable by amine residues, although the reactivity of these compounds appears to be less than that of our trinitro-compound. The chlorodinitrobenzenesulphonic acids of the Badische Co. (D.R.-P. 186989: Badische Anilin- und Soda-Fabrik) also react with amines, exchanging the chlorine atom for the amine residue, and so giving rise to the formation of substituted diphenylaminesulphonic acids. In all these cases, as in trinitroacetylaminophenol, the mobile nitro-group, or halogen atom, is ortho, and, in some instances, also para, with respect to other acid radicles present in the nucleus.

The Mobility of the Nitro-group in its Dynamical Aspect.

We may point out that the reactivity of trinitroacetylaminophenol promises to furnish an interesting case for study from the dynamical point of view, since by comparison with analogous compounds containing a mobile radicle the rate of elimination of the 3-nitro-group, if measurable, would give important information concerning the actual degree of mobility of particular sets of radicles due to their nature and position in connexion with the nature and position of the other radicles present in the nucleus. The development of the work in this direction necessitates the discovery of some method by which the course of the reactions can be followed quantitatively, and, as this may take much time for its realisation, it may be useful to indicate the general line of the proposed inquiry. To give an illustration of the kind of comparison contemplated, attention may be called to picryl chloride, trinitroanisole, and picrylmethylnitrosoamine:



In all three compounds the mobile radicle is in the same position with reference to the nitro-groups, and any reactions common to the series, if of measurable velocity, would enable the relative

"mobility" of the substituents Cl , $\text{O}\cdot\text{CH}_3$, and $\text{N}(\text{NO})\cdot\text{CH}_3$ to be expressed numerically. These compounds are, in fact, well known to react with amines with the formation of trinitro-secondary amines. Piceryl chloride was used by Wedckind in his studies on steric hindrance (*Ber.*, 1900, **33**, 426), and the interaction of piceryl-methylnitrosoamine and amines has been studied by Bamberger and Müller (*ibid.*, 100). It is of interest to note that in this last case the removal of the mobile group is preceded by the formation of an additive compound of the nitrosoamine and the amine. The elimination of the nitro-group from trinitroacetylaminophenol is also preceded by the formation of salts, the general formula of which is, presumably, $\text{C}_6\text{H}(\text{NO}_2)_3(\text{NHAc})\cdot\text{ONH}_3\text{R}'$ or



or some tautomeric form.

With respect to trinitroanisole, we may take the present opportunity of calling attention to the extreme reactivity of this compound towards certain amines. Thus with ammonia it forms picramide with such readiness that this method has for some years been in use in our laboratory as the most convenient process for preparing this substance in quantity. Trinitroanisole is readily prepared by the extreme nitration of anisolesulphonic acid by means of fuming nitric acid. On dissolving the pure trinitro-compound in alcohol, and adding alcoholic ammonia to the warm solution, an energetic reaction takes place, and in a few minutes the solution solidifies to a pulpy mass of crystals of pure picramide. This reactivity of the methoxy-group between ortho-substituents towards amines is being further investigated (compare the recently-published method of replacing the hydroxyl group in nitrated phenols by amine residues by Ullmann and Géza Nádaí, *Ber.*, 1908, **41**, 1870).

In the case of trinitroacetylaminophenol, the mobility of the nitro-group will most probably be measurable by determining the velocity of formation of the iminazoles. Before applying quantitative methods for this purpose, however, it was necessary to ascertain the special influence of the nature of the amine which is involved in the reaction, and an extended series of experiments has been carried out for this purposes, the results of which are summarised in the following section.

The Reactivity of the Trinitro-compound in Relation to Steric Hindrance.

The formation of substituted amines, secondary or tertiary, by the interaction of trinitroacetylaminophenol and primary or secondary amines may be regarded as a case of the formation of hetero-

catenic* compounds resulting from the linking of carbon and nitrogen atoms. From this point of view it is evident that the reaction might be expected to be subject to those protecting or retarding influences conveniently grouped in the present state of theoretical knowledge under the term "steric hindrance." Such protecting influence might, in the present case, be exerted in various ways, all referable ultimately to the special nature of the amine taking part in the reaction. With primary alkylamines, if heterocatenic systems are subject to the same law as homocatenic systems, the yield of iminazole might be expected to be influenced by the number of atoms which would form the chain in the intermediate product of the reaction in accordance with Bischoff's "dynamic hypothesis." The subject has not yet been investigated from this point of view, owing to practical difficulties connected with the quantitative method of determining the yield of iminazole, and, in fact, the longest chain at present synthesised is C-N-C-C, which is present in the intermediate compounds formed by the interaction of the trinitro-compound and ethylamine or benzylamine (see the former paper, *Trans.*, 1906, 89, 1935).

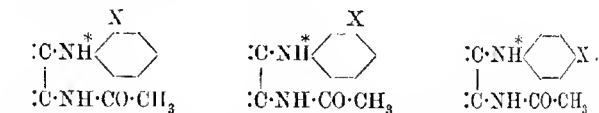
In the case of secondary amines, the size (or weight) of the radicles attached to the nitrogen atom might also be expected to influence the yield or to prevent any combination taking place at all. The experiments in this direction have not yet been carried very far, as the preliminary trials showed that the combination was restricted to dialkylamines (dimethylamine) and piperidine. No combination takes place with methylaniline, benzylaniline, diphenylamine, or carbazole. This result is of interest in connexion with the work of other investigators, as it brings out very clearly the relationship between the reactivity of the compound containing the mobile radicle and the special nature of this radicle (see preceding section). Thus Wedekind (*loc. cit.*) found that picryl chloride reacted to a considerable extent with methylaniline (65—70

* The terms "homocatenic" and "heterocatenic" are suggested as convenient expressions for open-chain systems composed respectively of similar and dissimilar atoms. They would be the analogues of the terms "homocyclic" and "heterocyclic," now generally used for the closed-chain systems. In the present case, we are really dealing with compounds of a mixed type, as one or both of the terminal carbon atoms form part of a ring system. No more confusion need arise, however, in such cases, than in those of cyclic compounds containing long "side chains." One objection to these terms, which will perhaps weigh heavily with many, is their hybrid character. Dr. P. Jacobson, with whom I have been in correspondence on the question, has suggested as alternatives the words "isostreptic" and "heterostreptic." The necessity for having some general terms descriptive of fundamental constitution being recognised, it may be left open for the present which of the proposed expressions shall finally be adopted. —R. M.

per cent. of catenation product), and that combination took place also with benzyaniline. With diphenylamine and carbazole negative results were obtained, as we found to be the case with our trinitro-compound.* It is evident from these experiments that the strongly negative halogen atom is capable of overcoming "steric hindrance" in cases where the mobile nitro-group fails. The extended researches of Bischoff with the esters of the bromo-fatty acids (see, for summary, Stewart's "Stereochemistry," p. 364, *et. seq.*), and of Menschutkin with alkyl bromide and the bromo-nitrobenzenes (*Ber.*, 1877, **30**, 2775, 2966; *J. Russ. Phys. Chem. Soc.*, 1897, **29**, 444), point to the same conclusion.

With substituted primary arylamines the protecting influence of ortho-substituents might be expected to make itself apparent in the yield of iminazole. Numerous quantitative experiments have been carried out with the object of determining how far the "iminazole condensation" could be relied on for giving concordant and dependable numerical data, and it has been found that substituted amines, containing acid radicles (halogens, nitro-group, hydroxyl, &c.), and the anisidines all gave satisfactory results. The homologues of aniline, however, did not give very concordant yields, and for the present purpose they may be disregarded. The practical details of the quantitative method are given in the experimental part, and the reasons for the irregularity of the results with the toluidines, ψ -cumidine, &c., are therein discussed.

Before submitting the quantitative results, it is necessary to point out that in the formation of an iminazole from a substituted arylamine by our method two independent influences are concerned. The first stage being a substituted diarylamine, the three following groupings are possible:



(X=substituent. Only the carbon atoms attached to the condensing ortho-chlorine are taken into consideration. For the sake of simplicity, only mono-substituted rings are represented.)

The formation of the diarylamine is governed by the usual "steric" influence. The formation of the iminazole ring might be expected to be influenced by the mobility of the hydrogen atom marked *, this being determined by the nature and position of

* Our experiments are not strictly comparable with Wedekind's from a quantitative point of view, as the reacting materials used by him were heated in sealed tubes, whereas the syntheses with trinitroacetylaminophenol were carried out under

the substituent X.* The practical effect of the greater or less mobility of this hydrogen atom would be to cause variations in the yield, due to the presence of more or less of the intermediate compound in the final product. In order to eliminate this source of error, the dried product, after being weighed, was submitted to a process for ensuring the complete conversion of any intermediate diarylamine into iminazole, and the correction thus given has been applied to each series of determinations. The details of this treatment are included in the description of the quantitative method given in the experimental part. The numbers given below for three sets of isomerides indicate the percentage of pure iminazole obtained calculated with reference to the yield theoretically obtainable. The results have been corrected for non-anhydridised compound, and are thus strictly comparable among themselves, as each determination was carried out under the same conditions. Wedekind's results (indicated by W) with picryl chloride and two sets of isomerides are also given for comparison.

Chloroanilines.

Ortho: (I) 87.5; (II) 87.3.	Mean, 87.4.	Corrected mean, 79.0.	W, 86.0.
Meta: (I) 87.3; (II) 87.3.	„ 87.3.	„ „ 80.6.	W, 88.9.
Para: (I) 91.8; (II) 91.8; (III) 92.	„ 91.86.	„ „ 88.74.	W, 92.5.

Nitroanilines.

Ortho: Nil.....			W, 5.3.
Meta: (I) 94.2; (II) 96.2.	Mean, 95.2.	No loss on anhydridisa-	
tion			W, 91.2.
Para: (I) 99.8; (II) 96.2.	„ 98.0.	„ „	W, 80.2.

Anisidines.

Ortho: (I) 90.9; (II) 90.2; (III) 90.4; (IV) 90.4.	Mean, 90.5.	Corrected mean, 79.0.	
Meta: (I) 92.5; (II) 93.8; (III) 94.2.	„ 93.5.	„ „	88.5.
Para: (I) 91.2; (II) 89.6.	„ 90.4.	„ „	85.7.

Determinations of yields with other sets of isomerides are in progress. With respect to the foregoing results, we may point out that the special influence of the ortho-substituent is very clearly shown in all three series. With chlorine as a substituent the order

the ordinary pressure as described in the experimental part of this paper. When no combination takes place between our trinitro-compound and an amine under these conditions, it is safe to assume that, at higher temperatures and pressures, any reaction that occurred would simply be the result of the decomposition of the trinitro-compound. The latter can be heated in methylamine solution to its decomposing point without the formation of any substituted phenyltolylamine.

* A special case is referred to in the experimental part in connexion with the iminazole from *m*-anisidine.

is the same as observed by Wedekind. With the nitroanilines, the special character of the mobile radicle is revealed by the negative result given by *o*-nitroaniline, as compared with the 5.3 per cent. obtained by Wedekind. The order of the yields with the meta- and para-isomerides is different from that given by picryl chloride, a result which may also be connected with the special character of the mobile radicle. With the methoxy-group as a substituent, the ascending order is the same as that given by picryl chloride for the nitro-group, namely, *o*-, *p*-, *m*-. The yield with *o*-chloroaniline is fairly large (79 per cent.), and it is of interest to note that when another ortho-substituent is present the steric hindrance is absolute, no combination taking place with 2:4:6-trichloro- or tribromoaniline. 2:4-Dinitroaniline, as might have been anticipated, also gave a negative result.

EXPERIMENTAL.

Method of Determining the Yield of Iminazole.

The possibility of utilising the formation of iminazoles as a quantitative method was suggested by observing that these compounds were perfectly definite, phenolic in character, and very slightly soluble in water. In order to satisfy ourselves that the loss due to solubility was for the present purpose a practically negligible quantity, determinations of the solubility of several iminazoles were made by dissolving a known weight in a measured volume of water by means of a few drops of sodium hydroxide, precipitating by hydrochloric acid, and collecting on a tared filter, washing with a measured volume of water, and weighing the dried precipitate. The following are the results:

Iminazole from aniline:	2.0018	lost	0.021	in	800 c.c. of water.
„ „ <i>p</i> -toluidine:	1.8978	„	0.043	„	750 „ „
„ „ ψ -cumidine:	1.8124	„	0.0252	„	750 „ „
„ „ <i>o</i> -anisidine:	2.055	„	0.017	„	750 „ „

These may be regarded as typical iminazoles; those containing acid radicles in the original arylamine nucleus are less soluble. In the actual determinations of yield the quantity of water never reached 750 c.c.

The quantitative results, selected series of which are given in the preceding section, are obtained by the following method. The trinitro-compound, purified by crystallisation from acetic acid, is accurately weighed (2 grams), and suspended in 30 c.c. of alcohol. The amine is then added in the proportion of three molecules to one

of the trinitro-compound, and the contents of the flask, after being well mixed by agitation, heated on a water-bath for two hours. As none of the amines used in these determinations are volatile in alcohol vapour, and as the flask is provided with a reflux condenser, no loss is incurred. At the termination of the period of cohobation the flask is removed from the water-bath, allowed to cool, and 10 c.c. of concentrated hydrochloric acid added. After thorough agitation, 200 c.c. of water are added, and the contents of the flask allowed to stand for at least twelve hours. The precipitate is then collected, and washed with water until all soluble compounds are removed. At this stage the precipitate consists of a mixture of the iminazole and diarylamine, and the products of the action of nitrous acid (from the eliminated nitro-group) on the excess of amine. These products, according to the nature of the amine, may be aminoazo-compounds, diazoamino-compounds, or simply the products of the action of boiling alcohol on the diazonium salts. Any excess of basic substances is removed in the acid filtrate. The iminazoles and diarylamines with which we have been dealing are all phenolic compounds, and are not sufficiently basic to form salts with the dilute acid employed, so that no loss is incurred in this way. In order to separate the phenolic from the non-phenolic constituents of the mixture, the precipitate is washed back into the flask, and extracted by repeated agitation with dilute alkali. After filtration, the iminazole, together with any intermediate product, is contained in the alkaline filtrate, which is always of an orange colour. The addition of hydrochloric acid causes the immediate precipitation of the product required, which is collected on a tared filter, dried, and weighed.

In the foregoing method there are three possible sources of error, each of which has been dealt with in the course of a very large number of experiments with different amines:

(1). Any trinitro-compound escaping combination through steric hindrance would be decomposed during the process of alkaline extraction, and the products, being phenolic in character, would be precipitated with the iminazole. This source of error we have satisfied ourselves to be quite negligible. A blank experiment carried out with 2 grams of trinitroacetylaminophenol, without the addition of any amine, gave no weighable quantity of precipitate on acidifying the alkaline extract.

(2). Any intermediate product (diarylamine) mixed with the iminazole would introduce a *plus* error. This is not serious, as the precipitate finally weighed consists in all cases of the iminazole to a preponderating extent. The difference in molecular weight

between the iminazole and the diarylamine also is not great. Thus the aniline iminazole differs from the corresponding diarylamine by only about six units. With substituted amines the difference is less.

Experiments on various methods of dehydrating the diarylamine so as to convert it into the iminazole have led to the conclusion that the conversion is most satisfactorily effected by boiling an aqueous solution of the sodium salt. The corrections applied in calculating the results given in the preceding section were obtained by boiling a weighed quantity of the dried mixed product in water with the addition of just sufficient sodium hydroxide to bring about solution. After boiling for an hour, the solution is allowed to cool, filtered, if necessary, and the iminazole precipitated by hydrochloric acid, collected, dried and weighed. This method of purification not only ensures the complete anhydridisation of the product, but also removes impurities due to the other source of error given below. We may add that heating with concentrated sulphuric acid or heating the dried product alone is a less satisfactory method of dehydrating for quantitative purposes.

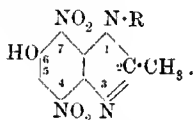
(3). Secondary products, resulting from the action of the eliminated nitro-group on the excess of amine, may pass through the filter with the alkaline extract, and so increase the weight of the final product by being precipitated with the iminazole. This is the most serious source of error, and is greatest in the case of the ortho-substituted amines, with which the yield of iminazole is least. We believe that the irregular results, varying in some cases as much as 10 per cent., given by the homologues of aniline, are mainly, if not entirely, due to this source. Thus, with *o*-toluidine and ψ -cumidine, the alkaline extract had generally to be passed several times through double filter papers before a clear solution could be obtained. For this reason we do not attach much weight for exact purposes to the determinations of yield given by these amines. With acid substituents, or the methoxy-group, in the aromatic nucleus of the amine, this source of error is much less pronounced, and, as shown by the numbers given, the results are fairly concordant. The alkaline method of treatment just described facilitates the removal of the last trace of impurity, especially after the mixed product has been dried. It is for this reason that the dried product has been treated in all cases where numerical accuracy was required, instead of adopting the more direct method of boiling the original alkaline solution obtained by the extraction of the crude product. That the quantity of impurity removed is directly proportional to the quantity of trinitro-compound that escapes combination is shown by the following numbers, obtained by subtract-

ing the corrected numbers from the original yields, and which therefore represent the actual loss undergone by each isomeride:

	Chloroanilines.	Anisidines.
Ortho	8.4	11.5
Meta	6.7	5.0
Para	3.12	4.7

How much of this loss is to be attributed to the admixed diarylamine cannot at present be estimated, but it is certainly insignificant as compared with the loss due to the removal of by-products.

The new benziminazoles prepared in the course of the present research are described below. In order to avoid repetitions of names and formulæ, the nomenclature is throughout simplified by the omission of the references to the positions of the methyl, the two nitro-, and the hydroxyl groups, all of which are unchanged throughout the series, the only variable substituent being that attached to the 1-N atom:



Dinitrohydroxy-1-phenylmethylbenziminazole.

This compound, which is readily formed by the interaction of aniline and the trinitro-compound, has been described in the former paper (Trans., 1906, **89**, 1939). To the statements there given we are now enabled to add the following.

The substance is of remarkable stability, resisting the action of concentrated sulphuric acid when heated with the latter until decomposition begins. On the other hand, the intermediate diarylamine, when heated to a high temperature with sulphuric acid, does not pass into the iminazole, but gives soluble products which have not yet been investigated. This observation was made in the course of experiments on methods of anhydridisation, and led to the adoption by preference of the alkaline method. The iminazole also resists fusion with alkali at a high temperature, and it does not undergo "azo-condensation" on heating with zinc dust and alkali, or with alkaline glucose. On partial reduction with ammonium sulphide it gives only amorphous products, and on complete reduction with tin and hydrochloric acid it yields a base of which the hydrochloride crystallises in stumpy needles, and which is no doubt the diaminoiminazole. The free base is rapidly oxidised on exposure to the air, and has not been isolated.

The hydroxyl group in this, and, in fact, in all the iminazoles of

the present series, is sufficiently protected by the neighbouring nitro-group to resist methylation by dimethyl sulphate and alkali. It benzoylates very imperfectly by the Schotten-Baumann method, but the product is so readily debenzoylated that a pure compound could not be obtained by crystallisation. On boiling for about two hours with acetic anhydride, an *acetyl* derivative was obtained, which crystallised from acetic acid in dense, colourless, transparent, hexagonal plates, melting at 206°*:

0.0968 gave 0.1916 CO₂ and 0.0359 H₂O. C=53.98; H=4.12.

0.1148 gave 15.75 c.c. N₂ (moist) at 13° and 746.1 mm. N=15.88.

C₁₆H₁₂O₆N₄ requires C=53.9; H=3.39; N=15.76 per cent.

The hydroxyl in this iminazole can be methylated by heating the silver salt with methyl iodide in alcoholic solution in the usual way. The methylation is, however, very imperfect, and the yield of methyl ether is small, owing to the protecting influence of the 7-nitro-group. The *silver* salt is best prepared by adding a solution of silver nitrate to a solution of the sodium salt of the iminazole. It is practically insoluble in cold water, and separates as an ochreous, amorphous precipitate. The *methyl* ether crystallises from alcohol in pale yellow, flat needles, melting at 205.5°:

0.0950 gave 13.7 c.c. N₂ (moist) at 12° and 760.6 mm. N=17.13.

C₁₇H₁₂O₅N₄ requires N=17.07 per cent.

The iminazole cannot be further nitrated by nitric acid alone, but a mixture of fuming nitric with concentrated sulphuric acid acts on the compound with the formation of a trinitro-derivative, consisting chiefly of an iminazole identical with that which can be directly synthesised from *m*-nitroaniline. The group represented by the 1-N atom and its attached complex thus belongs to the meta-orienting series.

The yield of iminazole from aniline under the conditions described is 84–91 per cent. of that theoretically obtainable.

Dinitrohydroxy-1-o-tolylmethylbenziminazole.

This compound was prepared from trinitroacetylaminophenol and *o*-toluidine by the general method. The product, after the usual treatment, was found to be very impure, many crystallisations from absolute alcohol being necessary before a definite compound could be isolated. A specimen of *o*-toluidine was specially purified by converting the purchased sample (Kahlbaum's) into picrate, crystal-

* The combustion of these iminazoles is very difficult to carry out satisfactorily, owing to the copious evolution of oxides of nitrogen. As no combustion of the original iminazole was given in the former paper, we may state that we have found: C=53.56; H=3.55, the formula C₁₄H₁₀O₅N₄ requiring C=53.5; H=3.18 per cent.

rising from alcohol until the melting point was constant (215°), basifying with alkali, and distilling with steam. This purified base, however, gave the same impure product, and there can be no doubt that steric hindrance by the methyl group causes the formation of compounds other than those resulting from direct catenation. These by-products are most difficult to separate from the iminazole. A direct determination of the loss undergone by the final product, after drying and boiling with alkali, showed that it contained about 3 per cent. of impurity.

The pure iminazole crystallises in ochreous scales, melting at $147-149^{\circ}$:

0.06376 gave 12.75 c.c. N_2 (moist) at 12° and 751.7 mm. $N=17.08$.

$C_{15}H_{12}O_3N_4$ requires $N=17.07$ per cent.

Silver salt: an orange, microcrystalline powder, insoluble in water:

0.0633 gave 7 c.c. N_2 (moist) at 13° and 746.3 mm. $N=12.81$.

0.2397 „ 0.0594 Ag. $Ag=24.79$.

$C_{15}H_{11}O_3N_4Ag$ requires $N=12.87$; $Ag=24.83$ per cent.

Ethyl ether: prepared from the silver salt and ethyl iodide; after repeated crystallisation from alcohol with animal charcoal, ochreous scales, melting at 153° :

0.1174 gave 15.4 c.c. N_2 (moist) at 12.5° and 775.7 mm. $N=15.85$.

$C_{17}H_{16}O_3N_4$ requires $N=15.76$ per cent.

Acetyl derivative: prepared by boiling the iminazole with acetic anhydride; crystallises from alcohol in brown, nodular crystals; melting point somewhat vague at about 139.5° :

0.2012 gave 25.65 c.c. N_2 (moist) at 9.5° and 759 mm. $N=15.29$.

$C_{17}H_{14}O_4N_4$ requires $N=15.17$ per cent.

The yield from *o*-toluidine is 71—72 per cent. of that required on the assumption that the final product consists of iminazole.

Dinitrohydroxy-1-p-tolylmethylbenziminazole.

Obtained from the trinitro-compound and *p*-toluidine. In this case, as with all the para-substituted amines, the formation of iminazole is more rapid than with the ortho-modification, and soon after the reaction has been started the crystalline deposit begins to separate from the hot solution. The pure compound crystallises from alcohol, in which it is but sparingly soluble, in large, ochreous scales with a silvery lustre, and melting at 204.5° :

0.1414 gave 20 c.c. N_2 (moist) at 12.5° and 761.6 mm. $N=17.03$.

$C_{15}H_{12}O_3N_4$ requires $N=17.07$ per cent.

Ammonium salt: orange needles, very insoluble in water.

Silver salt: ochreous, microscopic needles:

0.2590 gave 0.0642 Ag. Ag = 24.77.

$C_{15}H_{11}O_5N_4Ag$ requires Ag = 24.83 per cent.

Ethyl ether: from the silver salt and ethyl iodide; crystallises from alcohol in pale ochreous needles with a silky lustre; melting point 176.5°:

0.0937 gave 12.15 c.c. N_2 (moist) at 12° and 778.9 mm. N = 15.78.

$C_{17}H_{16}O_5N_4$ requires N = 15.76 per cent.

The yield of iminazole from *p*-toluidine averages about 87–88 per cent. of that required by theory.

Dinitrohydroxy-1-o-anisylmethylbenziminazole.

From the trinitro-compound and *o*-anisidine. Crystallises from alcohol in small, ochreous scales, melting at 193°:

0.0776 gave 10.6 c.c. N_2 (moist) at 14° and 768.1 mm. N = 16.24.

$C_{15}H_{12}O_6N_4$ requires N = 16.28 per cent.

Silver salt: orange, microcrystalline powder.

Methyl ether: pale yellow needles (from alcohol); melting point 168°:

0.2110 gave 27.9 c.c. N_2 (moist) at 12.5° and 759.3 mm. N = 15.64.

$C_{16}H_{11}O_6N_4$ requires N = 15.66 per cent.

Acetyl derivative: from the iminazole by boiling with acetic anhydride; crystallises from alcohol in dense, ochreous scales, melting at 162–163°:

0.1039 gave 12.8 c.c. N_2 (moist) at 9.5° and 752.4 mm. N = 14.64.

$C_{17}H_{14}O_7N_4$ requires N = 14.5 per cent.

Dinitrohydroxy-1-m-anisylmethylbenziminazole.

From the trinitro-compound and *m*-anisidine.* The product in this case was mixed with much colouring matter, probably the azo-compound resulting from the action of the eliminated nitro-group on the free base. After alkaline extraction and precipitation by acid, the product consisted obviously of a mixture of the iminazole and diarylamine. Anhydridisation was effected by heating with concentrated sulphuric acid on the water-bath, and also by the alkaline method. The pure compound is not very readily soluble

* Prepared by methylating the monoacetyl derivative of *m*-aminophenol by dimethyl sulphate and alkali, hydrolysing the product by sulphuric acid, basifying with alkali, distilling in steam, and finally purifying the oily product by fractional distillation.

in alcohol, and separates from this solvent, partly in ochreous, nodular aggregates, and partly as a light ochreous flocculent deposit. Both forms have the same melting point, 186° , with previous darkening at 146° :

0.0928 gave 13 c.c. N_2 (moist) at 17° and 755.2 mm. $N=16.14$.

$C_{16}H_{12}O_6N_4$ requires $N=16.28$ per cent.

The presence of the intermediate diarylamine in this case is of importance as indicating the lesser mobility of the hydrogen atom of the NH group when in the meta-position with respect to the other substituent in the amine nucleus (methoxy-group). The mobility of this hydrogen atom, which is concerned in the formation of the iminazole ring, will no doubt be found to follow the ortho-para rule.

Dinitrohydroxy-1-p-anisylmethylbenziminazole.

From the trinitro-compound and *p*-anisidine. Crystallises from alcohol in large, ochreous scales, melting at 198.5° :

0.1238 gave 16.65 c.c. N_2 (moist) at 11.5° and 774.3 mm. $N=16.3$.

$C_{15}H_{12}O_6N_4$ requires $N=16.28$ per cent.

Ammonium salt: small, red needles, sparingly soluble in cold water.

Silver salt: bright ochreous powder, insoluble in cold water:

0.1336 gave 13.9 c.c. N_2 (moist) at 14° and 774.4 mm. $N=12.39$.

0.1962 „ 0.0461 Ag. $Ag=23.55$.

$C_{15}H_{11}O_6N_4Ag$ requires $N=12.28$; $Ag=23.6$ per cent.

Methyl ether: pale yellow needles from alcohol; melting point $169-170^{\circ}$:

0.0689 gave 9.4 c.c. N_2 (moist) at 14° and 748.3 mm. $N=15.80$.

$C_{16}H_{14}O_6N_4$ requires $N=15.66$ per cent.

Dinitrohydroxy-1-o-chlorophenylmethylbenziminazole.

From the trinitro-compound and *o*-chloroaniline. Crystallises from alcohol in lustrous, pale yellow scales, melting at 240° :

0.1295 gave 17.7 c.c. N_2 (moist) at 16° and 742.1 mm. $N=16.26$

$C_{14}H_9O_5N_4Cl$ requires $N=16.1$ per cent.

Dinitrohydroxy-1-m-chlorophenylmethylbenziminazole.

Prepared, as usual, from *m*-chloroaniline. This compound was always found to crystallise from alcohol in two forms, nodular aggregates and ochreous scales, both having the same melting point, namely, $170-171^{\circ}$:

0.0837 gave 11.8 c.c. N_2 (moist) at 20° and 758.9 mm. $N=16.69$.

0.1565 „ 0.0662 AgCl. $Cl=10.27$.

$C_{14}H_9O_3N_4Cl$ requires $N=16.1$; $Cl=10.16$ per cent.

Dinitrohydroxy-1-p-chlorophenylmethylbenziminazole.

From *p*-chloroaniline, as before. Crystallises from alcohol in flat, pale ochreous needles, melting at 246° with decomposition:

0.0830 gave 11.1 c.c. N_2 (moist) at 11° and 760 mm. $N=16.03$.

0.2472 „ 0.0997 AgCl. $Cl=9.94$.

$C_{14}H_9O_3N_4Cl$ requires $N=16.1$; $Cl=10.16$ per cent.

Dinitrohydroxy-1-p-nitrophenylmethylbenziminazole.

o-Nitroaniline, as stated in the introductory part, forms no catenation product, with the trinitro-compound. The trinitro-compound readily reacts with *p*-nitroaniline, forming an iminazole but very slightly soluble in boiling alcohol, and crystallising from glacial acetic acid in ochreous scales, melting and decomposing at $249-250^\circ$:

0.1447 gave 24 c.c. N_2 (moist) at 16° and 754 mm. $N=19.54$.

$C_{14}H_9O_7N_5$ requires $N=19.54$ per cent.

The salts formed by this iminazole are so insoluble that they appeared worthy of special study, from the point of view of utilising them for analytical purposes. A number of quantitative determinations showed, however, that they offered no particular advantages.

Ammonium salt: crystallises from hot water in small, red scales, which do not dissociate to any considerable extent when dried in the water-oven:

0.0952 gave 18.2 c.c. N_2 (moist) at 19° and 756 mm. $N=21.65$.

$C_{14}H_{12}O_7N_6$ requires $N=22.38$ per cent.

Potassium salt: formed by dissolving the iminazole in a boiling aqueous solution of potassium carbonate, allowing to crystallise, and purifying by recrystallisation from water, in which it is but sparingly soluble: lustrous, red prisms containing no water of crystallisation:

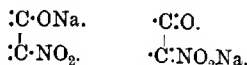
0.0933 gave 14.7 c.c. N_2 (moist) at 19° and 753 mm. $N=17.94$.

0.1803 „ 0.0386 K_2SO_4 . $K=9.62$.

$C_{14}H_8O_7N_5K$ requires $N=17.74$; $K=9.8$ per cent.

Sodium salt: this salt is of particular interest on account of its crystallising in two forms, namely, dense, red nodules and flat,

orange needles. The two kinds of crystals were generally, but not invariably, obtained together. It is possible that the "isonitro-automerism," to which attention has recently been turned, more especially through the researches of Hantzsch, may be realised in this iminazole, and that the two forms of sodium salt are represented:



We hope to be able to make a further study of the salt, as well as of the iminazole and its ethers, from this point of view:

0.2671 gave 0.0459 Na_2SO_4 . $\text{Na} = 5.57$.

0.1263 gave 20.25 c.c. N_2 (moist) at 18° and 761.7 mm. $\text{N} = 18.54$.

$\text{C}_{14}\text{H}_5\text{O}_7\text{N}_5\text{Na}$ requires $\text{Na} = 6.04$; $\text{N} = 18.4$ per cent.

Neither the potassium nor the sodium salt can be converted into ethers by direct alkylation.

Silver salt: dull orange, microcrystalline powder, practically insoluble in water. The dry salt deflagrates on heating.

Dinitrohydroxy-1-ψ-cumylmethybenziminazole.

From the trinitro-compound and ψ-cumidine. Crystallises from alcohol, in which it is very difficultly soluble, in minute, pale ochreous needles, melting at 237° :

0.1030 gave 13.8 c.c. N_2 (moist) at 14° and 763 mm. $\text{N} = 15.82$.

$\text{C}_{17}\text{H}_{16}\text{O}_5\text{N}_4$ requires $\text{N} = 15.76$ per cent.

The yield in this case showed a variation of from 78.2 to 91.6 per cent. of the theoretical quantity, this discrepancy being entirely due to the difficulty of removing the secondary products of the reaction. One of these products is ψ-cumene, formed, no doubt, by the action of the eliminated nitro-group on the free cumidine, and the decomposition of the diazonium salt by the boiling alcohol. The hydrocarbon tends to keep the product resinous, and interferes considerably with the processes of extraction and purification.

The products of the interaction of the trinitro-compound and secondary amines are still under investigation.

CITY AND GUILDS TECHNICAL COLLEGE,
FINSBURY.

CLXIV.—*Contributions to the Chemistry of the Cholesterol Group. Part I. The Action of Hydrogen Peroxide and of Fused Potassium Hydroxide on Cholesterol.*

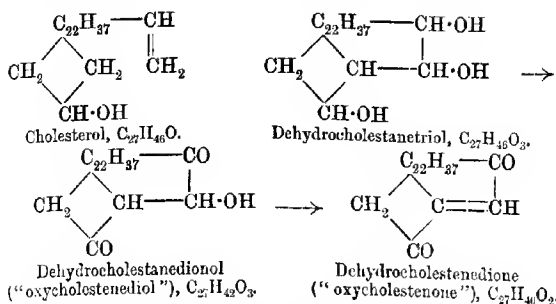
By ROBERT HOWSON PICKARD and JOSEPH YATES.

THE great difficulty which hinders the elucidation of the constitution of the unsaturated secondary alcohol, cholesterol, is that, although it is itself beautifully crystalline, the products of its oxidation are generally amorphous, and therefore not easy to separate and characterise. Owing to the high molecular weight and the difficulty always met with in the combustion of cholesterol and its derivatives, the empirical formula is somewhat uncertain. In the older literature, the formula $C_{26}H_{44}O$ is assigned to cholesterol, but the researches of Mauthner and Suida (*Monatsh.*, 1894, **15**, 362) showed that it contains twenty-seven carbon atoms in the molecule. Some uncertainty still attaches to the number of hydrogen atoms, for, whilst Mauthner and Suida give the formula $C_{27}H_{44}O$, later investigations, particularly those of Diels and Abderhalden (*Ber.*, 1904, **37**, 3092 *et seq.*), point to the formula $C_{27}H_{40}O$, which is adopted in this paper.

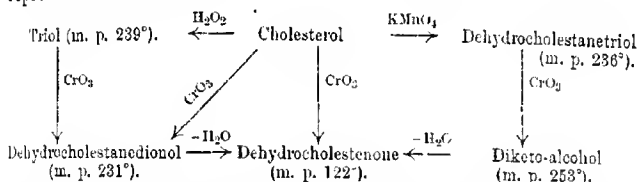
Mauthner and Suida (*Monatsh.*, 1896, **17**, 579) studied the oxidising action of chromic acid on cholesterol, and obtained in small quantities two compounds, which were named by them "oxycholestenediol" and "oxycholestenone," with the empirical formulæ $C_{27}H_{42}O_3$ and $C_{27}H_{40}O_3$ respectively. The latter, an unsaturated diketone, is obtained by the action of dehydrating agents on the former, which has been shown to be a diketo-alcohol by the researches of Windaus (compare *Ber.*, 1906, **39**, 2249). This investigator* has also shown that cholesterol has a terminal vinyl group in the molecule, and by its oxidation in benzene solution with potassium permanganate he has obtained a very small quantity of a compound, $C_{27}H_{40}O_3$, melting at 236° , which he names dehydrocholestanetriol, this, when further oxidised, yields a diketo-alcohol melting at 253° . This diketo-alcohol is isomeric with dehydrocholestanedionol, since dehydration converts it into dehydrocholestenediono, these names being the more systematic designations which Windaus gives to the two compounds obtained by Mauthner and Suida as described above.

From these and other results, Windaus formulates the first stages in the oxidation of cholesterol as follows, the formation of an intermediate aldehydic substance being assumed:

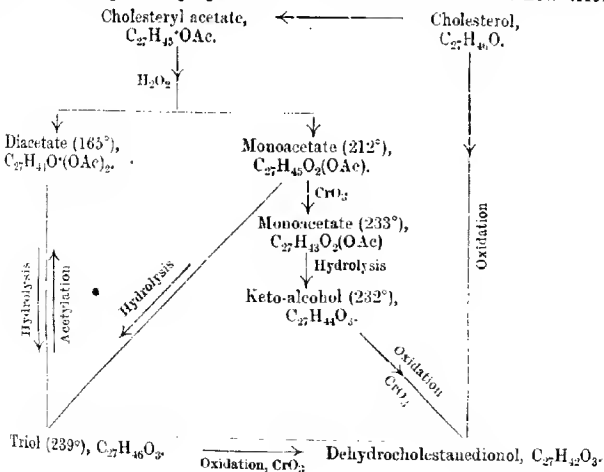
* Windaus has recently published (*Arch. Pharm.*, 1908, [ii], **246**, 117) an excellent summary of his own and other researches on cholesterol.



We have found that cholesterol can be oxidised by hydrogen peroxide to a "triol," melting at 239° , which is isomeric with that obtained as above by Windaus. When oxidised, this triol yields dehydrocholestanedionol; it contains the hydroxyl group of cholesterol, and when partly oxidised yields a monoketo-alcohol, $\text{C}_{27}\text{H}_{44}\text{O}_3$. The inter-relation of these reactions and those of Mauthner and Suida and Windaus can be represented as follows:



In the experimental part of this paper there is a description of several new compounds prepared to show the relation of this new triol



to cholesterol and dehydrocholestanedionol, the connexion between each being illustrated by the scheme on p. 1679.

These new reactions give approximately quantitative yields of the substances described, and therefore we regard our results as affording very strong confirmation of Windaus' formulation of the first oxidation products of cholesterol.

Action of Fused Potassium Hydroxide on Cholesterol.

Numerous experiments were carried out with a view to obtaining simple degradation products of cholesterol. The action of fused potassium hydroxide, however, only yields very small quantities of two crystalline products, these being the monobasic hydroxy-acid, $C_{26}H_{44}(OH) \cdot CO_2H$, and the dibasic acid, $C_{24}H_{42}(CO_2H)_2$.

EXPERIMENTAL.

Source of Cholesterol.

Some of the cholesterol used in these experiments was obtained from gall stones, whilst the remainder was supplied by Schuchardt, and had been obtained partly from gall stones and partly from brain substance. It all melted sharply at $146-147^\circ$, and was readily soluble in cold chloroform. The specific rotation of some cholesterol which had been prepared from a single gall stone, recrystallised once from alcohol, and dried at 90° , was $[\alpha]_D^{25} - 37.59^\circ$ (with $c=3.9$ in chloroform). The product from Schuchardt, after drying at 90° , had $[\alpha]_D^{25} - 38.77^\circ$ (with $c=5.0$ in chloroform), and, after three crystallisations from absolute alcohol and drying at 90° , had $[\alpha]_D^{25} - 38.01^\circ$ ($c=2.6$ in chloroform).

Some material used in earlier (1902) experiments contained (then undetected) traces of cholesteryl arachidate, which led us to believe (Proc., 1903, 19, 187) that cholesterol, when oxidised, yielded arachidic acid. We much regret this error, which has found its way into several text-books. Hydrolysis under pressure, repeated several times, is required to purify completely cholesterol and its allies.

Action of Hydrogen Peroxide on Cholesterol.

Preparation of a Neutral Substance, $C_{27}H_{46}O_3$.

As a result of very many preliminary experiments, it was found that, whenever cholesterol dissolved in acetic acid was treated with hydrogen peroxide, the product obtained was always more or less acetylated. It was therefore thought advisable to acetylate the cholesterol before submitting it to the action of the reagent, and this was then found to increase the yield considerably. The hydrogen

peroxide was used under conditions similar to those described by W. H. Perkin (Proc., 1907, 23, 166). A 20 per cent. solution of material in glacial acetic acid was treated with about one-sixth of its volume of 30 per cent. hydrogen peroxide (Merck's "perhydrol"). It may, however, be noted that the products are very similar whether the material is previously acetylated or not. The cholesteryl acetate used had been crystallised from acetic acid, and melted sharply at 113° .

The operation was performed as follows: 10 grams of cholesteryl acetate were dissolved in 50 c.c. of glacial acetic acid, and 10 c.c. of the hydrogen peroxide added. The mixture, when heated on a water-bath, first separated into two layers, the lighter oily layer gradually disappearing during the heating. Considerable effervescence ensued, probably due to excess of the peroxide, and the heating was continued for about two hours, when the action had apparently ended. When cool, a crystalline solid was deposited, which melted indefinitely at about 170° , the yield being nearly 50 per cent. The cautious dilution of the filtrate with water gave a further quantity. The crystalline solid thus obtained was not homogeneous, being a mixture of two substances, a monoacetate and a diacetate of the neutral substance, $C_{27}H_{46}O_3$. It was therefore dissolved in methyl alcohol and boiled for two or three hours with an excess of sodium methoxide. When the mixture was poured into water, the deacetylated product was precipitated, and, when dry, melted at about 230° . After crystallisation, first from benzene, in which both acetates are fairly soluble, and then from methyl alcohol, it was obtained in felted masses of long, lustrous needles melting at 239° .

It dissolves in the common organic media; it is, however, very sparingly soluble in chloroform or benzene, and even less so in light petroleum. It does not combine with bromine dissolved either in chloroform or acetic acid. On analysis:

0.1260 gave 0.3550 CO_2 and 0.1272 H_2O . C = 76.8; H = 11.2.

0.1224 „ 0.3457 CO_2 „ 0.1264 H_2O . C = 77.0; H = 11.0.

$C_{27}H_{46}O_3$ requires C = 77.5; H = 11.0 per cent.

Diacetate.—When the substance melting at 239° is boiled for thirty minutes with excess of acetic anhydride and a small quantity of fused sodium acetate, the diacetate was obtained in prismatic needles melting at 162° . After recrystallisation from methyl alcohol, it was obtained in lustrous, long, prismatic needles, which melted at 165° .

It is soluble in the common organic media, and, when deacetylated with a methyl-alcoholic solution of sodium methoxide, yields the original substance:

0.1206 gave 0.3289 CO_2 and 0.1161 H_2O . C = 74.4; H = 10.7.

$C_{31}H_{50}O_5$ requires C = 74.1; H = 10.0 per cent.

When boiled with a known excess of sodium methoxide, 1.6900 neutralised the equivalent of 0.2500 NaOH. The calculated amount for two acetyl groups is 0.2693 NaOH. Cryoscopic determinations of the molecular weight in benzene solution indicated the formula $C_{31}H_{50}O_5$.

The diacetate was also prepared directly from the product obtained from the cholesteryl acetate. This latter was extracted with warm light petroleum. After removal of the petroleum, the crude extract melted at about 140° , and, after two crystallisations from methyl alcohol, yielded the pure diacetate, melting at 165° .

Monooacetate.—The residue insoluble in light petroleum, from the extraction described above, melted at about 200° . It was crystallised three times from ethyl alcohol, and obtained in small, glistening needles melting at 212° . It is soluble in the common organic media, with the exception of light petroleum:

0.1374 gave 0.3774 CO_2 and 0.1333 H_2O . $C = 74.9$; $H = 10.8$.

$C_{29}H_{48}O_4$ requires $C = 75.6$; $H = 10.4$ per cent.

When boiled with excess of sodium methoxide, 0.5512 neutralised the equivalent of 0.0552 NaOH. The calculated amount for $C_{29}H_{48}O_4$ is 0.0479 NaOH.

The product from this hydrolysis, after one crystallisation from methyl alcohol, melted at 239° .

When the monoacetate was boiled with acetic anhydride and a little fused sodium acetate, it yielded the diacetate melting at 165° .

Dipropionate.—The dipropionate was prepared by boiling the substance with twice its weight of propionic anhydride for two hours. When cool, the compound crystallised in long, slender needles. After recrystallisation from methyl alcohol, it melted sharply at 172° .

When boiled with a known excess of sodium methoxide, 0.0980 neutralised the equivalent of 0.0158 NaOH. The calculated amount for $C_{33}H_{54}O_5$ containing two propionyl groups is 0.0149 NaOH.

Action of Hydrogen Peroxide on Dicholesteryl Ether.

To obtain further confirmation of the course of the reaction between hydrogen peroxide and cholesterol, a few experiments with dicholesteryl ether (Manthner and Suida, *Monatsh.*, 1896, 17, 29) were carried out. Owing to the insolubility of the ether in acetic acid, the experiments were performed in benzene solution. The neutral substance thus obtained was acetylated and then crystallised from a mixture of benzene and methyl alcohol. In this way, a diacetate was obtained in long, prismatic needles melting at 143° .

When boiled with a known excess of sodium ethoxide, 0.5120

neutralised the equivalent of 0.0454 NaOH. The calculated amount for $C_{55}H_{99}O_7$ with two acetyl groups is 0.0453 NaOH.

A cryoscopic determination of the molecular weight was made :

0.1245 in 13.843 benzene gave a depression of 0.15° . M.W. = 1002.

$C_{58}H_{96}O_7$ requires M.W. = 904.

The product, after deacetylation, was crystallised twice from acetic acid, and obtained in small nodules of indefinite shape, which melted at 192° .

Owing to the description by Minovici (*Ber.*, 1908, **41**, 1561) of isomeric dicholesteryl ethers, further experiments in this direction have been postponed.

Preparation of the Keto-alcohol, $C_{27}H_{44}O_3$.

Oxidation of the Monoacetyl Derivative of $C_{27}H_{46}O_3$.

Four grams of the monoacetate (m. p. 212°) were dissolved in 60 c.c. of warm glacial acetic acid, and then mixed with a solution of 0.65 gram of chromium trioxide in 10 c.c. of 90 per cent. acetic acid.

This mixture was warmed on the water-bath for fifteen minutes, and then poured into water. The dried precipitate was then boiled with acetic anhydride for thirty minutes to convert any unoxidised material into the diacetate (m. p. 165°). The excess of acetic anhydride was then decomposed by water, and the precipitate dried and extracted with light petroleum, in which the diacetate is soluble.

The portion insoluble in light petroleum was deacetylated by boiling with a methyl-alcoholic solution of sodium methoxide. After crystallisation from methyl alcohol, the keto-alcohol was obtained in long, slender needles, which had a pearly lustre and melted at 232° :

0.1196 gave 0.3392 CO_2 and 0.1193 H_2O . C = 77.5 ; H = 11.1.

$C_{27}H_{44}O_3$ requires C = 77.9 ; H = 10.6 per cent.

Acetyl Derivative.—This was obtained as described above, and represents the portion insoluble in light petroleum. It is very sparingly soluble in methyl alcohol, from which it crystallises in long needles melting at 233° .

When boiled with a known excess of sodium methoxide, 1.4527 neutralised the equivalent of 0.1276 NaOH. The calculated amount for $C_{25}H_{40}O_4$ is 0.1269 NaOH.

Phenylhydrazone.—The keto-alcohol readily yielded a phenylhydrazone when warmed with an alcoholic solution of phenylhydrazine containing a few drops of acetic acid, from which it was deposited in yellow spangles, which melted at 162° . After recrystallisation from

ethyl alcohol, it was obtained in long, orange-yellow needles, which melted at 164°

0.2140 gave 10.7 c.c. N_2 (moist) at 20° and 766 mm. $N = 5.7$.

$C_{33}H_{50}O_2N_2$ requires $N = 5.5$ per cent.

Formation of Dehydrocholestanedionol by Oxidation of the Triol
(m. p. 239°) and the Keto-alcohol (m. p. 232°).

A solution of 4.2 grams of the alcohol (m. p. 239°) in 160 c.c. of 90 per cent. acetic acid was mixed with a cold solution of 4.2 grams of chromium trioxide in 40 c.c. of 90 per cent. acetic acid, and the mixture allowed to stand for twenty-four hours. The crystalline deposit was then filtered and extracted with 96 per cent. alcohol. The least soluble portion was crystallised from absolute alcohol, and obtained in beautiful long needles, which melted and decomposed at 231° .

An analogous experiment with the keto-alcohol (m. p. 232°) and half the quantity of chromium trioxide gave the same substance, the properties of which coincide with those of dehydrocholestanedionol (oxycholestenediol) described by Mauthner and Suida (*loc. cit.*).

The identity of this substance with "oxycholestenediol" was proved by its conversion into "dehydrocholestenedione" (oxycholestenone) and the preparation of the phenylhydrazone of the latter.

The "dionol" dissolved in chloroform solution was treated with dry hydrogen chloride for one hour, when the solution became milky. The mixture was then washed with sodium carbonate solution, dried, and the chloroform removed by distillation. The residue, after two crystallisations from ethyl alcohol, melted at $121-122^{\circ}$, and with phenylhydrazine yielded the very characteristic insoluble hydrazone, which was obtained in golden-yellow spangles, melting at 271° . Mauthner and Suida (*loc. cit.*) give 122° as the melting point of oxycholestenone and 271° as the melting point of its phenylhydrazone.

Fusion of Cholesterol with Potassium Hydroxide.

The object of these experiments was to obtain degradation products of cholesterol which could be purified by crystallisation. Preliminary trials were carried out using a nickel crucible, which was subsequently discarded for an iron one. The addition to the fusion of small quantities of sodium peroxide, iron filings, or zinc dust did not seem to affect the yield of crystalline substances.

The method adopted finally was as follows: 6 grams of cholesterol were fused at a low temperature with 12 grams of potassium hydroxide in an iron crucible. The potassium hydroxide was first dissolved in a very small quantity of water, in which the cholesterol was suspended.

and the mixture heated. After the water was expelled, the mixture was constantly stirred, and the heating continued for some hours. The mass was next dissolved in water, acidified, and extracted six times with ether. The acid products were removed by washing the ethereal solution with very dilute sodium carbonate solution. The alkaline solution was then acidified and extracted with ether. A mixture of acids was thus obtained, which readily solidified in an evacuated desiccator after removal of the ether.

Acid, $C_{27}H_{45}O_3$.

When the mixture of acids is dissolved in hot ethyl acetate, a small crop of crystals is deposited. The yield may be increased by evaporation of the solvent, or by the addition of ethyl nitrate. The amount obtained from 6 grams of cholesterol never exceeded 0.3 gram. The acid can be recrystallised from ethyl acetate in small prisms, which melt at 241° :

0.1272 gave 0.3602 CO_2 and 0.1273 H_2O . $C = 77.2$; $H = 11.0$.

$C_{27}H_{46}O_3$ requires $C = 77.5$; $H = 11.0$ per cent.

The acid is insoluble in water and benzene, sparingly soluble in acetone and methyl alcohol, and soluble in hot acetic acid, acetic anhydride, and ether. The solution in acetic acid does not decolorise a solution of bromine in the same solvent. It readily dissolves in a warm dilute solution of sodium carbonate, and, when cooled, deposits a gelatinous salt. Potassium permanganate solution is not decolorised by an aqueous solution of the sodium salt. A dilute neutral solution of the acid in ammonia gives white, gelatinous precipitates, insoluble in hot water, with solutions of the acetates of calcium, barium, magnesium, zinc, cadmium, and lead.

The silver salt is also gelatinous, and consequently difficult to purify.

The empirical formula of the acid and the presence of one hydroxyl and one carboxyl group were proved by the preparation of the acetyl derivative and the ethyl ester.

Acetyl Derivative, $C_{29}H_{45}O_4$.

When the acid was boiled for about fifteen minutes with an excess of acetic anhydride, in which it is very soluble, and then poured into water, the acetyl derivative slowly separated out in hard, horny masses. It crystallised from aqueous alcohol in warty aggregates of prismatic crystals, which melted at 163° and decomposed about 200° .

A specimen, dried in the air, gave on analysis:

0.1253 gave 0.3328 CO_2 and 0.1216 H_2O . $C = 72.4$; $H = 10.7$.

0.1109 lost 0.0042 at 105° . $H_2O = 3.78$.

$C_{29}H_{48}O_4 \cdot H_2O$ requires C=72.8; H=10.5; $H_2O=3.76$ per cent.

$C_{28}H_{48}O_4 \cdot H_2O$ „ C=72.1; H=10.3; $H_2O=3.86$ „

A specimen, dried in the desiccator until constant in weight, was dissolved in warm alcohol and titrated with $N/10$ NaOH, using phenolphthalein as indicator:

0.1970 gram was neutralised by 0.0172 gram NaOH.

$C_{26}H_{44}OAc \cdot CO_2H$ requires 0.0171 gram NaOH.

Ethyl Ester, $C_{29}H_{50}O_2$.

The acid was shaken with ethyl alcohol saturated with hydrogen chloride for about eight hours.

Most of the alcohol and the hydrogen chloride was removed in an evacuated desiccator, the residue poured into water, and the ester extracted with ether. It is very soluble in the common organic solvents, except methyl and ethyl alcohols. It crystallised from the former solvent in twinned plates with a pearly lustre, and melted at 62° . A three per cent. solution in ether gave $[\alpha]_D$ about $+27^\circ$:

0.1222 gave 0.3496 CO_2 and 0.1235 H_2O . C=78.02; H=11.23

$C_{29}H_{50}O_2$ requires C=78.0; H=11.2 per cent.

$C_{28}H_{50}O_2$ „ C=77.4; H=11.5 „

Dibasic Acid, $C_{26}H_{44}O_4$.

The acid products from the fusion were treated with ethyl acetate and ethyl nitrate, as described above, to remove the acid $C_{27}H_{48}O_4$. The residues were heated on the water-bath to remove all traces of the solvents, then macerated with light petroleum, and filtered. The portion insoluble in the petroleum, crystallised from glacial acetic acid in clusters of small needles, which melted at 190° :

0.1364 gave 0.3700 CO_2 and 0.1314 H_2O . C=74.0; H=10.7.

$C_{26}H_{44}O_4$ requires C=74.2; H=10.4 per cent.

$C_{27}H_{44}O_4$ „ C=75.0; H=10.1 „

The acid is soluble in ethyl acetate, benzene, chloroform, or alcohol. Its solution in sodium carbonate does not decolorise potassium permanganate in the cold, and its solution in acetic acid does not decolorise a solution of bromine in acetic acid.

0.1284 Gram of acid, dissolved in ethyl alcohol, was titrated with $N/10$ NaOH, and neutralised 0.0236 NaOH; indicating for a dibasic acid a molecular weight of 436, that of $C_{26}H_{44}O_4$ being 420.

The neutral solution of the ammonium salt gave white, amorphous precipitates, insoluble in hot water, with solutions of the acetates of calcium, barium, zinc, cadmium, magnesium, and lead.

The silver salt is amorphous; a specimen, dried at 100° , was analysed, when

0.1552 gave 0.2800 CO_2 , 0.0981 H_2O , and 0.0523 Ag. $\text{C} = 49.2$;
 $\text{H} = 7.0$; $\text{Ag} = 33.7$.

$\text{C}_{26}\text{H}_{42}\text{O}_4\text{Ag}_2$ requires $\text{C} = 49.2$; $\text{H} = 6.9$; $\text{Ag} = 34.0$ per cent.

The thanks of the authors are due to Drs. A. S. Barnes and J. Hunt for the presentation of some specimens of gall stones, and also to the Research Fund Committee of the Society for grants which have defrayed the cost of some of the material used in this work.

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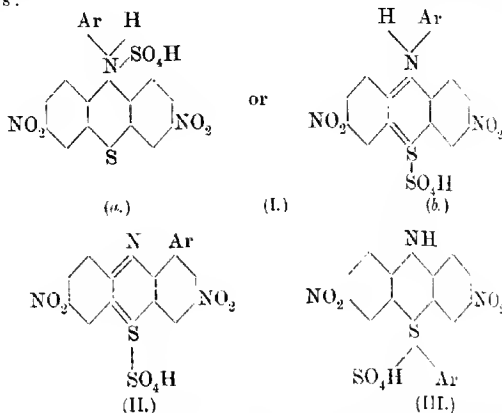
(CLXV.—*Derivatives of S-Phenylphenazothionium.* *Part II.*

By SAMUEL SMILES and THOMAS PERCY HILDITCH.

IN our first communication on this subject (Trans., 1908, 93, 145), the products obtained by condensation of phenetole with di-*p*-nitrodiphenylamine sulphoxide and its methyl derivative were described. From the previous observation, that aromatic sulphoxides yield sulphonium salts in this reaction, and from the study of the properties of the condensation products, it was shown that the latter are derivatives of S-phenylphenazothionium. The investigation of this group has now been extended to the substances obtained by condensation of phenol with both the dinitrodiphenylamine sulphoxides described by Bernthsen (*Annalen*, 1885, 230, 116) and to the amino-derivatives of the group. Before dealing with these substances in particular, it may be remarked that, besides the reasons already given for assuming them to contain the S-phenylphenazothionium structure, further evidence of this may be obtained from a general standpoint.

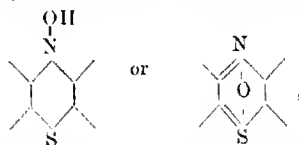
From di-*p*-nitrodiphenylamine sulphoxide and phenetole with concentrated sulphuric acid, a green sulphate is obtained, which is readily hydrolysed by water to a crimson, fluorescent base. By treating the sulphate with alkali hydroxide, sulphuric acid is eliminated with formation of a deep red, fluorescent anhydro-base. Now in the condensation of aromatic compounds with thiodiphenylamine oxide, it is clear that the aryl group may unite with the benzothiazine system in either of three ways: it may be attached to nitrogen (I), or to a benzene nucleus

(II), or its sulphur (III), and the sulphate would then be represented as follows:



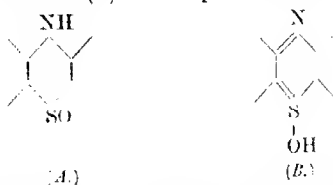
It may be noted that a substance of formula II would differ from I and III by two hydrogen atoms less, but the difference would not greatly affect the results of analysis.

The first alternative (Ia and Ib) involves the improbable assumption that the thiodiphenylamine oxide contains either the structure



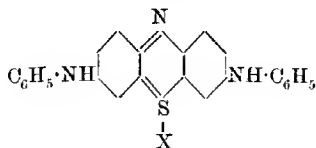
but apart from this it is evident that, in either case, removal of hydrazid from the salt by alkali hydroxide must yield an *N*-arylthiodiphenylamine, and this is contrary to experience. Hence this structure must be discarded.

On a priori grounds, the second formula seems more probable. For various reasons, which need not here be mentioned, it is probable that the sulphoxide structure (A) is the pseudo-form of the quinonoid



sulphonium base (B), into which it is converted by the action of acids. This being the case, the dinitro-sulphoxide on being dissolved in con-

centrated sulphuric acid previous to condensation would be changed to the quinonoid sulphonium salt. Now, since Kehrman (*Annalen*, 1902, 322, 1) has shown that these ortho-quinonoid derivatives combine with aniline in presence of oxidising agents, giving compounds of the type



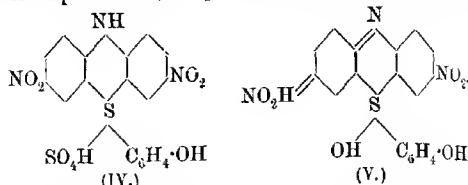
(where X is an acid radicle), it might be considered possible that in the reaction in question a substance of type II might be formed in a similar manner by simultaneous removal of hydrogen from the aromatic nucleus of phenol and the dinitrophenazothionium salt. Accordingly, the process would be one of oxidation and not of dehydration. This view, however, is untenable. If it were correct, it is clear that, since no special oxidising agent is introduced, the oxidation must take place at the expense of the sulphuric acid or of part of the dinitro-sulphoxide. In the former circumstance, sulphurous acid would be formed, but we have not been able to detect traces of this even when dealing with large quantities of material. Further, if the sulfoxide served as an oxidising agent, half of it would appear in the product as dinitrothiodiphenylamine, and this, also, we have not been able to isolate. Moreover, the sulphate is produced in excellent yield—about 90 per cent. of the theoretical. Further evidence that the reaction is one of dehydration and not of oxidation is afforded by the fact that it does not take place without dehydrating agents, even if oxidising agents are present. Thus, when a solution of di-*p*-nitrodiphenylamine sulfoxide in phenetole is warmed with ferric chloride, the green sulphate in question is not formed. Similar negative results have been found with acid alcoholic solutions of the sulfoxide with phenetole or aniline and ferric chloride. Against this formula (II) may also be set the facts that :

1. The green salts are not attacked by sulphurous acid in alcoholic solution, whereas under these conditions the ortho-quinonoid dibenzophenazothionium bromide is readily reduced.

2. It is difficult to imagine how a substance of formula II could by the action of alkali hydroxide lose the elements of hydracid to form the anhydro-base.

For these reasons the second formula is excluded, and there remains as the only possibility the third, which we have already shown is entirely in accordance with the properties of the substance and is to be anticipated from the nature of the reaction from which it is formed.

By condensing phenol with di-*p*-nitrodiphenylamine sulphoxide in presence of sulphuric acid, the green salt (IV) has now been obtained.



It is readily hydrolysed by hot water or by dilute aqueous sodium carbonate to the corresponding red hydroxy-derivative (V). The base prepared in this manner is not homogeneous; it consists for the greater part of a sparingly soluble red base, mixed with a very small quantity of a more soluble purple base, which is isomeric with the former. The most probable explanation of this isomerism is that in the two substances the phenolic hydroxyl group occupies different positions relatively to the sulphur atom. They would thus be formed by ortho- and para-condensation of the thionyl group with phenol, and it may be noted that this has been already observed (Smiles and Le Rossignol, *Trans.*, 1906, 89, 705) in the condensation of phenetyl sulphoxide with phenetole, where two isomeric triphenetylsulphonium salts are formed. It may be supposed that the less soluble isomeride is the para-, and the more soluble is the ortho-derivative, but in the absence of definite proof we prefer respectively to term them the α - and β -derivatives.

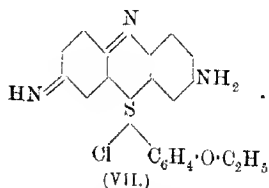
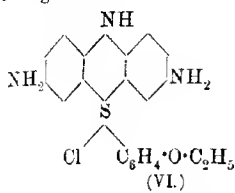
By ethylation with ethyl sulphate in alkaline solution, the less soluble or α -phenolic base is converted into an ethyl derivative which has the same composition as the product previously obtained from phenetole and di-*p*-nitrodiphenylamine sulphoxide. However, the substances prepared by the two methods are not identical. That obtained by ethylation of the α -phenolic base is distinguished from the isomeride by its slighter solubility and the different tint of its solution in concentrated hydrochloric acid. The contrast between the isomerides may be summarised as follows:

Dinitro-S-phenetylphenazothionium Hydroxide.

	By ethylation of a phenolic base.	By condensation with phenetole.
Solution in concentrated hydrochloric acid is	Yellowish-green.	Deep bluish-green.
And when ammonia is added it changes to	Rose-red with orange fluorescent.	Purplish-red.
When this is set aside	Rose-red base completely precipitated, the solution becoming colourless.	Purplish-red base is partly precipitated.

The more soluble or β -phenolic base very closely resembles the phenetole condensation product of which it is probably the parent substance; but we are unable to offer decisive proof of this, since the quantity of the β -isomeride available was so small that the product of ethylation could not be closely studied.

By the reduction of dinitro-*S*-phenetylphenazothionium chloride, the pale yellow diamino-derivative (VI) is formed, and this, on being oxidised with ferric chloride or atmospheric oxygen, is transformed to the deep-blue chloride (VII), to which the quinonoid structure must be assigned:



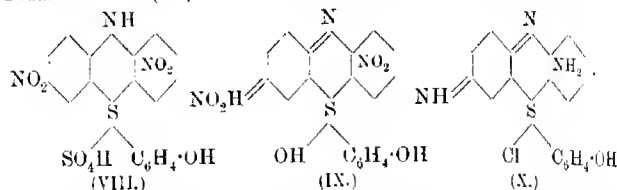
For shortness' sake, substances of this type (VII) may be referred to as derivatives of *S*-phenylthionine, although it may be noted that Kehrman (*Ber.*, 1897, **30**, 1571; 1901, **34**, 4170) has shown that thionine probably contains the ortho-quinonoid arrangement. The hydroxide corresponding with the above chloride is precipitated from solutions of the latter on the addition of aqueous alkali hydroxide as a purplish-brown powder. Other salts, such as the picrate, dichromate, and platinichloride, may be obtained. The chlorides of *S*-phenetyl- and β -hydroxyphenyl-thionine are sparingly soluble in hot water; the solutions impart a bluish-grey tint to silk or cotton fabrics.

It is worth noting that these amino-sulphonium bases are perceptibly stronger than those of the previously described dinitro-series. The chloride of dinitro-*S*-phenetylphenazothionium is readily hydrolysed by hot water or by cold aqueous solutions of sodium acetate or carbonate; *S*-phenetylthionine chloride, however, is not attacked by these reagents, and the base is only liberated by the action of aqueous sodium hydroxide or boiling aqueous solutions of alkali carbonate. It is therefore clear that the basicity of the quadrivalent sulphur in these compounds is influenced by the nature of the groups substituted in the benzothiazine nucleus. Kehrman (*Ber.*, 1906, **39**, 914) has arrived at a similar conclusion from a study of derivatives of the ortho-quinonoid phenazothionium. It will be shown in the next and concluding communication on this group that with four nitro-groups the molecule may assume acidic properties.

Derivatives of isoDinitrodiphenylamine Sulphoxide. — Bernthsen *Annalen*, 1885, **230**, 116) has shown that nitration of thiodiphenyl-

amine yields di-*p*-nitrodiphenylamine sulphoxide, together with a more soluble isomeric substance, which may be termed *isodinitrodiphenylamine sulphoxide*. That the latter substance contains the thionyl group, follows from reasons similar to those advanced in the case of the less soluble isomeride (Bernthsen, *loc. cit.*, and Smiles and Hilditch, *Trans.*, 1908, 93, 145). It thus follows that the isomerism depends on the different positions occupied by the nitro-groups. Bernthsen showed that in the less soluble isomeride the two nitro-groups occupy the 3:9-positions,* but the constitution of the *isosulphoxide* is at present undetermined.

*iso*Dinitrodiphenylamine sulphoxide, when condensed with phenol, yields an olive-green sulphate (VIII), which may be hydrolysed to an Indian-red base (IX):



By oxidising the diamino-derivative which is obtained by reduction of the dinitro-salts (VIII), a deep blue dyestuff (X) is formed, the properties of which are similar to those of the dipara-compounds (VII). It seems probable therefore that in the sulphoxide one nitro-group is in the para-position with respect to the imino-group, but at present there is no evidence to show the position of the other nitro-group. An attempt to decide this question by synthesis of the sulphoxide is being made by one of us.

It may be remarked that the hydroxide of *isodinitro-S*-hydroxyphenylphenazothionium is not fluorescent, in distinction from the isomeric di-*p*-nitro-derivative. In other physical properties, the two series closely resemble one another.

EXPERIMENTAL.

Derivatives of Dinitro-S-hydroxyphenylphenazothionium.

The condensation of di-*p*-nitrodiphenylamine sulphoxide with phenol in presence of concentrated sulphuric acid was effected by a process similar to that previously described (*Trans.*, 1908, 93, 150) with phenetole and the same sulphoxide. On pouring the acid mixture into water, the green sulphate of 3:9-dinitro-*S*-hydroxyphenylphenazothionium was precipitated. This was collected and thoroughly washed

* In Part I (*loc. cit.*), the position of the nitro-groups was called 3:3', instead of 3:9.

with water, and it was then converted into the hydroxide by trituration with excess of cold aqueous sodium carbonate. The brown solid was then separated from the alkaline liquor and treated with boiling water to separate the α - and β -bases; the total yield of these was 5.3 grams from 5 grams of the sulphoxide. The more soluble β -hydroxide dissolved in the hot medium, forming a purple solution, which was filtered from the less soluble α -hydroxide. On cooling the filtrate, β :3:9-dinitro-S-hydroxyphenylphenazothionium hydroxide was precipitated as a purple, crystalline powder. It was collected, and, after further purification, was analysed; a sample which had been dried in the steam-bath gave the following numbers:

0.1364 gave 0.2702 CO_2 and 0.0456 H_2O . $\text{C}=54.01$; $\text{H}=3.71$.

$\text{C}_{18}\text{H}_{13}\text{O}_6\text{N}_3\text{S}$ requires $\text{C}=54.14$; $\text{H}=3.26$ per cent.

The substance melts at $206-208^\circ$, and in ethereal solution exhibits an intense green fluorescence. A portion of this hydroxide was converted into the *chloride*. The latter is a deep green powder, which readily dissolves in concentrated hydrochloric acid, giving a bluish-green solution; it is sparingly soluble in cold absolute alcohol, the colour of the solution being blue:

0.0907 gave 0.1725 CO_2 and 0.0241 H_2O . $\text{C}=51.86$; $\text{H}=2.95$.

$\text{C}_{18}\text{H}_{12}\text{O}_6\text{N}_3\text{ClS}$ requires $\text{C}=51.75$; $\text{H}=2.88$ per cent.

α -Derivatives.

The insoluble residue left after removal of the β -hydroxide with hot water consists of the α -hydroxide in an almost pure state. The substance was further purified by precipitation with ether from acetone solution.

α :3:9-Dinitro-S-hydroxyphenylphenazothionium hydroxide was thus obtained as a chocolate-coloured powder, which melted at $218-220^\circ$. It is sparingly soluble in boiling water, and very soluble in cold aqueous alkali hydroxide; the solutions in these media are wine-red and rose-red respectively, and neither exhibits fluorescence. The ethereal and alcoholic solutions are fluorescent:

0.1341 gave 0.2665 CO_2 and 0.0397 H_2O . $\text{C}=54.20$; $\text{S}=3.29$.

0.1953 " 0.1207 BaSO_4 , $\text{S}=8.48$.

$\text{C}_{18}\text{H}_{13}\text{O}_6\text{N}_3\text{S}$ requires $\text{C}=54.14$. $\text{H}=3.26$; $\text{S}=8.01$ per cent.

The *chloride* is a deep green powder, which is very sparingly soluble in absolute alcohol or concentrated hydrochloric acid with a yellowish-green colour:

0.1268 gave 0.2393 CO_2 and 0.0357 H_2O . $\text{C}=51.46$; $\text{H}=3.12$.

0.1943 " 0.0650 AgCl . $\text{Cl}=8.27$.

$\text{C}_{18}\text{H}_{12}\text{O}_6\text{N}_3\text{ClS}$ requires $\text{C}=51.75$; $\text{H}=2.88$; $\text{Cl}=8.50$ per cent.

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The *platinichloride* was obtained by mixing an alcoholic solution of the chloride with aqueous chloroplatinic acid. If the proportions of the reagents are adjusted so that precipitation takes place slowly, the substance may be obtained in green, crystalline scales, which decompose with frothing at 223°. Epichlorohydrin furnishes a crimson solution, from which ether precipitates the platinichloride as a green powder. A sample which had been purified in this manner was analysed :

0.1805 gave 0.0291 Pt. Pt = 16.12.

$(C_{18}H_{12}O_5N_3S)_2PtCl_6$ requires Pt = 16.64 per cent.

The solutions in alcohol exhibit dichroism.

The *picrate* is an olive-brown powder, which, on being heated, turns green, and, finally, decomposes indistinctly at about 180°:

0.1366 gave 0.2364 CO_2 and 0.0338 H_2O . C = 47.21; H = 2.75.

$C_{18}H_{11}O_5N_3S_2C_6H_3O_7N_3$ requires C = 47.21; H = 2.29 per cent.

The *dichromate* is precipitated as an olive-green powder when an acid solution of the chloride is added to aqueous potassium dichromate. The substance does not melt below 240°:

0.1180 gave 0.0186 Cr_2O_3 . Cr = 10.79.

$C_{30}H_{24}O_{17}N_6S_2Cr_2$ requires Cr = 10.61 per cent.

Ethylation of the α -Hydroxide.

α -3:9-Dinitro-S-phenetylphenazothionium Hydroxide.—Three grams of the sulphate of the α -base were dissolved in excess of 10 per cent. aqueous alkali hydroxide. Small quantities of ethyl sulphate were added to this from time to time, and after each addition the contents of the flask were thoroughly shaken. The mixture was maintained at 50—60° by means of a water-bath, and during the process a copious precipitate was formed, the end of the reaction being indicated by the pale red colour of the supernatant liquid. When this condition was reached, the solid was collected, then washed with ether to remove adherent ethyl sulphate, and finally triturated with dilute aqueous sodium hydroxide. The product was again collected, and then well washed with cold water; when dry it weighed two grams. Further purification furnished *α -3:9-dinitro-S-phenetylphenazothionium hydroxide* as a crimson-brown powder, which melted at 207—208°. The base is sparingly soluble in cold concentrated hydrochloric acid, giving a yellowish-green solution, which, on treatment with excess of aqueous sodium hydroxide, turns at first rose-red with a bright orange fluorescence, and, then, after the lapse of about an hour, yields a rose-red precipitate of the original substance. This behaviour, as already mentioned in the theoretical part of the paper, is distinct from that of the phenetyl-

sulphonium base which is obtained from phenetole and the dinitro-sulphoxide. The α -S-phenetyl derivative is almost insoluble in boiling water:

0.1044 gave 0.2160 CO_2 and 0.0372 H_2O . $\text{C} = 56.43$; $\text{H} = 3.96$.

0.2226 „ 0.1257 BaSO_4 . $\text{S} = 7.75$.

$\text{C}_{20}\text{H}_{17}\text{O}_6\text{N}_3\text{S}$ requires $\text{C} = 56.21$; $\text{H} = 3.98$; $\text{S} = 7.50$ per cent.

Benzoylation of the α -Hydroxide.

On submitting the α -hydroxide to the usual process of aqueous alkaline benzoylation, the benzoyl derivative was precipitated as an insoluble, reddish-brown powder. This was collected, and several attempts to purify it with various solvents were made, but in each case the benzoyl derivative decomposed, regenerating the α -hydroxide and benzoic acid or its anhydride. This behaviour has previously been observed with the benzoyl derivatives of simpler phenolic thietines (Barnett and Smiles, *Proc.*, 1908, **24**, 123); for example, phenoxydiphenylsulphonium, on benzoylation, yields benzoic anhydride, the originally formed benzoyl derivative not being sufficiently stable to be isolated.

Amino-derivatives.

S-Phenetylthionine.—The chloride of dinitro-*S*-phenetylphenazothonium is reduced in alcoholic solution with zinc dust and hydrochloric acid. The finely-powdered chloride is covered with about eight or ten times its weight of absolute alcohol; to this mixture concentrated hydrochloric acid is added, and then the zinc dust in small portions. The mixture must be kept well stirred, otherwise the reaction is apt to be hindered by the caking together of the chloride and zinc dust. As the reduction proceeds, the chloride passes into solution, and the liquid assumes a yellow tint. Finally, the excess of zinc dust is removed, and, on pouring the clear solution into a large volume of cold water, a colourless precipitate of the chloride of the diamino-derivative is obtained. This is readily converted by atmospheric oxygen into the dyestuff, but the oxidation may be more rapidly effected by the addition of a few c.c. of concentrated aqueous ferric chloride. By adding a saturated solution of common salt, *S-phenetylthionine chloride* is precipitated, and may be purified by renewed solution and precipitation. When dry, the substance forms a deep blue powder with a metallic lustre; it is insoluble in ether, but soluble in water and in dilute mineral acids. Concentrated aqueous solutions exhibit dichroism; the dilute are dull blue with a red fluorescence. Silk is dyed a slate-grey by this substance.

Analysis showed that the air-dried compound contains three molecules of water of crystallisation, two of which are expelled at 100° ;

0.3256 air-dried substance lost 0.0262 H_2O . $\text{H}_2\text{O} = 8.0$.

$\text{C}_{20}\text{H}_{18}\text{ON}_3\text{ClS}, 3\text{H}_2\text{O}$ requires $2\text{H}_2\text{O} = 8.2$ per cent.

Elementary analysis was conducted with a sample dried at 100° to constant weight:

0.1205 gave 0.2644 CO_2 and 0.0552 H_2O . $\text{C} = 59.85$; $\text{H} = 5.09$.

0.1021 „ 0.2229 CO_2 „ 0.0482 H_2O . $\text{C} = 59.54$; $\text{H} = 5.25$.

0.1161 „ 0.0705 BaSO_4 . $\text{S} = 8.34$.

0.1251 „ 10.6 c.c. N_2 at 19.5° and 750 mm. $\text{N} = 9.9$.

$\text{C}_{20}\text{H}_{18}\text{ON}_3\text{ClS}, \text{H}_2\text{O}$ requires $\text{C} = 59.78$; $\text{H} = 4.98$; $\text{S} = 7.97$;
 $\text{N} = 10.46$ per cent.

S-Phenetylthionine hydroxide is precipitated as a purplish-brown powder by the addition of aqueous sodium hydroxide to a solution of the chloride. It is insoluble in water and sparingly so in ether, to which it imparts a pale violet tint. Solutions in alcohol are pure-coloured, but without fluorescence:

0.1556 gave 0.3759 CO_2 and 0.0789 H_2O . $\text{C} = 65.88$; $\text{H} = 5.64$.

0.1004 „ 0.2408 CO_2 „ 0.0496 H_2O . $\text{C} = 65.33$; $\text{H} = 5.50$.

$\text{C}_{20}\text{H}_{19}\text{O}_2\text{N}_3\text{S}$ requires $\text{C} = 65.75$; $\text{H} = 5.21$ per cent.

The *platinichloride* is a blue powder insoluble in water:

0.2248 gave 0.0390 Pt. $\text{Pt} = 17.36$.

$(\text{C}_{20}\text{H}_{18}\text{ON}_3\text{S})_2\text{PtCl}_6$ requires $\text{Pt} = 17.66$ per cent.

The *dichromate* is a dark green powder:

0.3623 gave 0.0600 Cr_2O_3 . $\text{Cr} = 11.34$.

$\text{C}_{40}\text{H}_{36}\text{O}_9\text{N}_6\text{S}_2\text{Cr}_2$ requires $\text{Cr} = 11.40$ per cent.

S-Hydroxyphenylthionine.—To prepare this substance, the chloride of α -dinitro-*S*-hydroxyphenylphenazothionium was reduced with zinc dust and hydrochloric acid by the same method as described for *S*-phenetylthionine.

S-Hydroxyphenylthionine chloride is sparingly soluble in cold water, but readily so in the hot medium; the dilute solutions are blue and the more concentrated, violet in colour, especially when hot. Solutions in alcohol are blue with a red fluorescence. After being heated at 100° until constant weight is attained, the substance retains one molecule of water:

0.2177 gave 0.4604 CO_2 and 0.0852 H_2O . $\text{C} = 57.68$; $\text{H} = 4.35$.

0.1150 „ 0.2441 CO_2 „ 0.0491 H_2O . $\text{C} = 57.90$; $\text{H} = 4.73$.

0.1412 „ 0.0888 BaSO_4 . $\text{S} = 8.64$.

0.2010 „ 0.0794 AgCl . $\text{Cl} = 9.75$.

$\text{C}_{18}\text{H}_{14}\text{ON}_3\text{ClS}, \text{H}_2\text{O}$ requires $\text{C} = 57.82$; $\text{H} = 4.28$; $\text{S} = 8.57$;

$\text{Cl} = 9.50$ per cent.

The air-dried substance contains water, but apparently not in any definite molecular proportion :

0.5776 lost at 100° $0.0444 \text{ H}_2\text{O}$. $\text{H}_2\text{O} = 7.7$

$\text{C}_{18}\text{H}_{14}\text{ON}_3\text{SCl}, 2\text{H}_2\text{O}$ requires $1\text{H}_2\text{O} = 4.6$ per cent.

$\text{C}_{18}\text{H}_{14}\text{ON}_3\text{SCl}, 3\text{H}_2\text{O}$ „ $2\text{H}_2\text{O} = 8.8$ „

This chloride may be converted into the corresponding hydroxide by means of cold aqueous sodium hydroxide or a hot solution of sodium carbonate, but the former reagent dissolves the base, forming the sodium salt. *S-Hydroxyphenylthionine hydroxide* was therefore prepared by digesting the chloride with a 10 per cent. aqueous solution of sodium carbonate at 60° . The base was purified by dissolving in alcohol and precipitating the solution with ether. When dry, the substance forms a brown powder, which is readily soluble in aqueous sodium hydroxide, sparingly so in hot water, and very slightly so in ether; the solution in the latter medium is a pale violet and not fluorescent. It is readily soluble in alcohol. At 100° , this hydroxide retains one molecule of water :

0.1842 gave 0.4314 CO_2 and $0.0800 \text{ H}_2\text{O}$. $\text{C} = 63.86$; $\text{H} = 4.83$.

$\text{C}_{13}\text{H}_{13}\text{O}_2\text{N}_3\text{S}, \text{H}_2\text{O}$ requires $\text{C} = 64.09$; $\text{H} = 4.45$ per cent.

The tinctorial properties of the salts of this base are similar to those of the previously described phenetyl derivative.

Experiments on the action of various alkaline reagents with the chloride were made by shaking the aqueous solution of the latter with the reagent in question, the mixture being covered with ether. The formation of the base was indicated by the violet tint of the ethereal layer. The results are summarised below :

Reagents (aqueous).	Result.
Sodium acetate (cold)	No base formed.
„ (hot)	„ „ „
Sodium carbonate (cold)	„ „ „
„ (hot)	Base formed.
Ammonia (cold)	Base formed, but partly dissolved.
Sodium hydroxide (cold)	Base formed, but completely dissolved as phenolic sodium salt.

Derivatives of isoDinitro-S-phenylphenazothionium.

isoDinitro-S-hydroxyphenylphenazothionium.—The sulphate of this base was obtained by condensing isodinitrodiphenylamine sulfoxide with phenol by means of cold concentrated sulphuric acid. The method employed was similar to that described in a former paper (Trans., 1908, 93, 145) for the condensation of phenetole with the isomeric *p*-dinitrodiphenylamine sulfoxide. The end of the reaction is indicated by the formation of a yellowish-green precipitate when a test-portion of the liquid is added to water. The acid liquid, on being

poured into a large bulk of cold water, yields a copious precipitate of *isodinitro-S-hydroxyphenylphenazothionium sulphate*. The yield is almost theoretical. This substance is an olive-green powder, very sparingly soluble in cold water, and moderately so in hot alcohol. Like the other dinitro-derivatives of this group, it is easily hydrolysed by boiling water to the parent base. To prepare the latter, the sulphate is triturated with warm aqueous sodium carbonate, the solid is then collected, and washed with cold water until the filtrate is no longer alkaline towards litmus. It is then dried, and finally purified by frequent precipitation from acetone solution with ether. When prepared in this manner, *isodinitro-S-hydroxyphenylphenazothionium hydroxide* is obtained as an Indian-red powder, which melts somewhat indistinctly at 195—197°. It is readily soluble in aqueous sodium hydroxide, alcohol, or chloroform, and slightly so in hot water or ether. The solutions are reddish-brown, but none are fluorescent, and the substance is thus sharply distinguished from the isomeric di-p-nitro-derivative, which, in ethereal solution, exhibits a fluorescence of peculiar brilliance :

0.1800 gave 0.3586 CO_2 and 0.0554 H_2O . $\text{C} = 54.34$; $\text{H} = 3.42$.

0.1000 „ 0.0613 BaSO_4 . $\text{S} = 8.40$.

$\text{C}_{18}\text{H}_{13}\text{O}_6\text{N}_3\text{S}$ requires $\text{C} = 54.14$; $\text{H} = 3.26$; $\text{S} = 8.00$ per cent.

The *chloride* has physical properties similar to those of the sulphate. When heated to 100°, it turns dark green, and then contains one molecule of water. A sample dried to constant weight at that temperature was analysed :

0.1006 gave 0.1824 CO_2 and 0.0318 H_2O . $\text{C} = 49.45$; $\text{H} = 3.59$.

$\text{C}_{18}\text{H}_{12}\text{O}_5\text{N}_3\text{ClS}\cdot\text{H}_2\text{O}$ requires $\text{C} = 49.61$; $\text{H} = 3.22$ per cent.

At a higher temperature, about 150°, the substance again undergoes a change, the remaining molecule of water being expelled ; at 205—210°, it melts with frothing. A solution of the chloride in aqueous alcohol exhibits a green and brown dichroism, which is probably due to partial hydrolysis, since it vanishes on the addition of mineral acid.

The *picrate* is a yellowish-green substance, which melts at 130°. The aqueous-alcoholic solution is orange in colour, indicating hydrolysis to the base and picric acid :

0.1253 gave 0.2148 CO_2 and 0.0304 H_2O . $\text{C} = 46.76$; $\text{H} = 2.30$.

$\text{C}_{18}\text{H}_{11}\text{O}_5\text{N}_3\text{S}\cdot\text{C}_6\text{H}_5\text{O}_7\text{N}_3$ requires $\text{C} = 47.21$; $\text{H} = 2.29$ per cent.

Reduction of the chloride of the above-mentioned nitro-compound with zinc dust and hydrochloric acid in the usual manner, and subsequent oxidation with ferric chloride of the diamino-derivative which is formed, gives the dark blue *S-hydroxyphenylisothionine chloride*. The substance, when crushed, exhibits a metallic lustre ; it imparts a blue colour to alcohol, in which it is freely soluble ; water is tinted a

reddish-violet. It may be noted that neither solution is fluorescent. The air-dried substance contains water, which is not completely expelled by prolonged exposure to a temperature of 100° . After being heated at this temperature until constant weight was reached, a sample retained three molecules of water for every two of the chloride:

0.1389 gave 0.2883 CO_2 and 0.0590 H_2O . $\text{C} = 56.63$; $\text{H} = 4.72$.

0.1061 „ 0.2190 CO_2 „ 0.0461 H_2O . $\text{C} = 56.28$; $\text{H} = 4.83$.

$\text{C}_{18}\text{H}_{14}\text{ON}_3\text{ClS}, 1\frac{1}{2}\text{H}_2\text{O}$ requires $\text{C} = 56.46$; $\text{H} = 4.44$ per cent.

S-Hydroxyphenylisothionine hydroxide may be prepared by treating the finely-powdered chloride with aqueous sodium carbonate at about 50° . This compound is deep purple in colour, and is soluble in the usual organic media or in aqueous sodium hydroxide, to which it imparts a reddish-brown tint. As with the chloride, the water is incompletely expelled at 100° :

0.1750 gave 0.4010 CO_2 and 0.0698 H_2O . $\text{C} = 62.48$; $\text{H} = 4.43$.

$\text{C}_{18}\text{H}_{15}\text{O}_2\text{N}_3\text{S}, \frac{1}{2}\text{H}_2\text{O}$ requires $\text{C} = 62.43$; $\text{H} = 4.62$ per cent.

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CLXVI.—A Reaction Distinguishing Phosphoprotein from Nucleoprotein and the Distribution of Phosphoproteins in Tissues.

By R. H. ADERS PLIMMER and F. H. SCOTT.

Two years ago one of us, in conjunction with Bayliss (*J. Physiol.*, 1906, 33, 439), observed that caseinogen when treated with one per cent. sodium hydroxide at 37° was decomposed in such a way that the whole of its phosphorus (except for a negligible quantity) was eliminated as inorganic phosphoric acid. This observation has now been extended to the other well-defined phosphoprotein, namely, vitellin of egg-yolk, which was found to behave in an exactly similar manner to caseinogen under the influence of one per cent. sodium hydroxide at 37° . It seemed possible, therefore, that the action of one per cent. sodium hydroxide at 37° for twenty-four hours might serve as a simple means of distinguishing between phosphoproteins and nucleoproteins.

Nucleoalbumins, or phosphoproteins as they are now termed, have been stated to occur in various tissues. As no one has succeeded in isolating these substances from such tissues, we have made use of the

above reaction for testing various organs for phosphoprotein. Before the reaction of one per cent. sodium hydroxide could be put to any such use, its action on the other organic phosphorus compounds, namely, lecithin, glycerophosphoric acid, and nucleic acid, in the tissues had to be determined. These compounds did not yield inorganic phosphoric acid when submitted to the action of one per cent. sodium hydroxide at 37°, as was expected from the known methods of preparation of glycerophosphoric acid from lecithin by boiling with baryta, and of nucleic acid from tissues by Neumann's method, which consists in heating the tissue to 70--80° with sodium hydroxide.

Besides these compounds, inorganic phosphates are also present in tissues, and, on account of their presence, the direct application of the reaction led to no positive result. An increase in the amount of inorganic phosphoric acid was always observed, but this was due rather to the solution of the tissue in the alkali, with the consequent liberation of phosphoric acid, than to the decomposition of phosphoprotein.

Consequently, a method of examining tissues had to be devised. This consisted in coagulating the tissue with alcohol, thoroughly extracting the lecithin with alcohol and ether, and then treating the coagulated protein with one per cent. sodium hydroxide at 37°, after the inorganic phosphates had been removed by repeated extraction with very dilute acid. By this method, also, determinations of the amount of the various kinds of phosphorus contained in the tissues can be made. The pancreas alone of the tissues so examined was found to contain phosphoprotein; the amount of phosphorus thus present amounted to 3 per cent. of the total phosphorus.

The experiments have also been extended to the ova of fishes, from which the substances ichthulin, icthbin, etc., have been isolated; these are regarded as phosphoproteins. Their presence was confirmed by this method.

The principal distribution of phosphoproteins thus appears to be in those substances which form the food-stuffs of the embryo bird and fish and the young mammal.

EXPERIMENTAL.

I. Separation of Phosphorus from Vitellin.

A. *Action of One per cent. Sodium Hydroxide.*—The vitellin employed in these experiments was either prepared by the usual method or by that described by Osborne and Campbell in 1900 (see Plimmer, *Trans.*, 1908, 93, 1500).

Experiment 1.—Five grams of vitellin were suspended in 200 c.c. of water, and 50 c.c. of *N*-sodium hydroxide were added. The mixture

was placed in an incubator at 37°, and from time to time samples of known volume (50 c.c.) were withdrawn with a pipette and precipitated by an equal volume of tannic acid solution; the soluble phosphorus was estimated in a known volume of the filtrate by Neumann's method as modified by Plimmer and Bayliss (*J. Physiol.*, 1906, **33**, 439). At the same time, other samples of 50 c.c. were removed and acidified by a known volume of acid; in the filtrate from the precipitate formed by the addition of acid, the inorganic phosphoric acid was estimated as magnesium pyrophosphate by precipitation with ammonium magnesium citrate. The complete precipitation of inorganic phosphoric acid by this method was previously demonstrated by Plimmer and Bayliss, and has been repeatedly verified during the course of these experiments (see below). All values so obtained were then calculated for the 50 c.c. sample, the total quantity of P_2O_5 in the mixture being estimated in a special sample of 10 c.c.

Time.	Soluble P_2O_5 (milligrams).	Inorganic P_2O_5 (milligrams).
0	—	—
24 hours	21.6	17.4
48 "	22.1	17.6
Total.....	22.8	

Experiments 2 and 3.—In these experiments, 5 grams of vitellin were treated with 525 c.c. of one per cent. sodium hydroxide at 37°. The vitellin dissolved slowly, and in three hours had not completely passed into solution. Samples of 100 c.c. were withdrawn at intervals, and precipitated by 2 c.c. of glacial acetic acid. In the filtrate from the precipitate formed by the addition of the acid, the soluble phosphorus was estimated by Neumann's modified method, and the inorganic phosphoric acid as magnesium pyrophosphate. The total P_2O_5 was estimated in a special sample of 10 c.c. All values calculated for 100 c.c. sample.

EXPERIMENT II.			EXPERIMENT III.		
Time.	Soluble P_2O_5 (milligrams).	Inorganic P_2O_5 (milligrams).	Time.	Soluble P_2O_5 (milligrams).	Inorganic P_2O_5 (milligrams).
0	10.4	0.5	0	1.6	0
15 hours	23.3	24.5	7 hours	22.6	20.4
24 "	28.4	25.3	24 "	24.0	23.5
41 "	29.7	24.5	48 "	25.2	24.8
4 days	31.0	26.6	11 days	27.2	24.5
Total ...	34.2		Total ...	26.6	

B. Action of One per cent. Hydrochloric Acid.—Just as in the case of caseinogen, the action of one per cent. and 4 per cent. hydrochloric acid differs markedly from that of one per cent. alkali on vitellin. No inorganic phosphoric acid is formed, and only after many days is the phosphorus in caseinogen completely separated in a soluble form.

Five grams of vitellin were treated with 500 c.c. of water and 15 c.c. of concentrated hydrochloric acid at 37°. Samples of 100 c.c. were removed at intervals and filtered; the soluble P_2O_5 and inorganic P_2O_5 were estimated in known volumes of the filtrates by the above-described methods. All values calculated for 100 c.c. sample.

One per cent. Hydrochloric Acid.			Four per cent. Hydrochloric Acid.		
Time.	Soluble P_2O_5 (milligrams).	Inorganic P_2O_5	Time.	Soluble P_2O_5 (milligrams).	Inorganic P_2O_5
0	0	0	0	2.8	0
18½ hours	trace	0	1 day	8.2	0
5 days	10.1	0	4 days	25.2	0
86 "	31.1	0	20 "	23.1	0
105 "	34.2	0	31 "	25.4	0
Total ...	33.6		Total ...	27.9	

An experiment carried out with caseinogen in exactly the same manner, in which the acidity was 1.3 per cent., gave the values:

Time.	Soluble P_2O_5 (milligrams).	Inorganic P_2O_5
0	trace	0
20 hours	"	0
2 days	5.1	0
6 "	3.8	0
24 "	9.5	0
Total.....	35.5	

We thus see that both vitellin and caseinogen are very stable towards acid, whereas they are decomposed by one per cent. alkali in such a way that the whole of the phosphorus is separated as inorganic phosphoric acid. The small residue which remains, just as in the case of caseinogen, seems to be due to the presence of nuclein or nucleoprotein in the vitellin employed.

C. *Action of Pepsin.*—It was of interest to examine the behaviour of vitellin and of caseinogen to pepsin; just as with acid, no inorganic phosphoric acid is formed, and the solution of the phosphoprotein takes place slowly.

(a)			(b)		
10 grams vitellin + 1000 c.c. 0.4 per cent. HCl + 0.1 gram pepsin.			20 grams caseinogen + 850 c.c. 0.4 per cent. HCl + 0.2 gram pepsin.		
Time.	Soluble P_2O_5 (milligrams).	Inorganic P_2O_5	Time.	Soluble P_2O_5 (milligrams).	Inorganic P_2O_5
0	0	0	0	7.0	0
25 hours	0	0	20 hours	13.9	0
2 days	0	0	28 "	15.8	0
68 "	8.2	0	2 days	15.2	0
Total...	14.6		6 "	18.4	0
			24 "	20.3	0
			Total...	34.2	

II. Separation of Phosphorus from Nucleic Acid and Nucleoprotein.

It is well known that nucleic acid is very resistant to the action of alkali. Neumann's method for preparing nucleic acid consists in heating the tissue to 70–80° with 3 per cent. sodium hydroxide in the presence of sodium acetate for half an hour to two hours, depending on the variety of nucleic acid which is required.

It was, however, necessary for the purpose of distinguishing between phosphoprotein and nucleoprotein to investigate the action of acid and alkali on nucleic acid and nucleoprotein in the same way as with caseinogen and vitellin.

Experiment 1.—Fifty c.c. of a solution of sodium nucleate prepared by Neumann's method from testis were mixed with 50 c.c. of 10 per cent. sodium hydroxide and kept at 37°. Samples of 10 c.c. were withdrawn at intervals, and tested for inorganic phosphate by ammonium magnesium citrate. The total P_2O_5 in the solution was estimated by Neumann's modified method. The results are tabulated below.

Experiment 2.—Fifty-two c.c. of the same solution of sodium nucleate were treated with 15 c.c. of concentrated hydrochloric acid and 37 c.c. of water at 37°. Samples of 5 c.c. were withdrawn at intervals and precipitated by an equal volume of tannic acid, and the soluble P_2O_5 was estimated by Neumann's modified method in the filtrate. At the same time, samples of 10 c.c. were removed and precipitated by ammonium magnesium citrate for inorganic phosphoric acid. Values calculated for 5 c.c. sample. Total P_2O_5 estimated in 5 c.c. sample.

EXPERIMENT I.		EXPERIMENT II.		
Time.	Inorganic P_2O_5 (milligrams).	Time.	Soluble P_2O_5 (milligrams).	Inorganic P_2O_5 (milligrams).
0	? trace	0	—	—
24 hours	? trace	24 hours	—	trace
5 days	? trace	44 "	—	trace
Total	13.6	5 days	9.6	1.9
		12 "	10.4	4.0
		Total ...	13.1	

Experiment 3.—One gram of nucleic acid prepared by Levene's method from herring testis was treated with 270 c.c. of one per cent. sodium hydroxide at 37°. Samples of 50 c.c. were withdrawn at intervals and tested for inorganic phosphate by ammonium magnesium citrate. Total P_2O_5 in 10 c.c. was estimated by Neumann's modified method. The results given below are calculated for 50 c.c. samples.

Experiment 4.—One gram of the same nucleic acid was treated with 250 c.c. of *N*-hydrochloric acid at 37°. Samples of 50 c.c. were removed and tested for inorganic phosphate. Total P_2O_5 by Neumann's modified method,

EXPERIMENT III.

Time.	Inorganic P_2O_5 .
0	0
24 hours	0
48 „	0
3 days	0
5 „	0
Total = 15.2 milligrams.	

EXPERIMENT IV.

Time.	Inorganic P_2O_5 .
0	0
2 days	0
4 „	0
8 „	0
Total = 15.8 milligrams.	

Experiment 5.—A solution of nucleoprotein (testis) in ammonia was treated with an equal volume of 10 per cent. sodium hydroxide at 37° . Samples were removed at intervals and precipitated by an equal volume of tannic acid, and the soluble P_2O_5 was estimated in the filtrate. Other samples were removed and tested with ammonium magnesium citrate for inorganic P_2O_5 .

Experiment 6.—One hundred and fifty c.c. of the same solution of nucleoprotein were neutralised and treated with 50 c.c. of hydrochloric acid and 100 c.c. of water at 37° . Samples were removed and filtered. Soluble P_2O_5 and inorganic P_2O_5 were estimated in the filtrate by the usual methods.

EXPERIMENT V.

Time.	Soluble P_2O_5 (milligrams).	Inorganic P_2O_5 .
0	0.0	0
24 hours	5.9	0
5 days	5.7	0
12 „	6.5	0
Total	7.2	

EXPERIMENT VI.

Time.	Soluble P_2O_5 (milligrams).	Inorganic P_2O_5 (milligrams).
0	—	—
4 days	6.6	2.4
11 „	—	3.7
Total	6.7	

In another experiment, an aqueous extract of testis was freed from lecithin and inorganic phosphates and treated with an equal volume of 2 per cent. sodium hydroxide. The soluble nucleic acid present in the solution was not decomposed in five days with the formation of inorganic phosphoric acid.

These experiments thus definitely show that there is a distinct difference in the behaviour of vitellin and caseinogen and of nucleic acid and nucleoprotein to one per cent. sodium hydroxide. The former are unstable, the latter stable. On the other hand, nucleic acid and nucleoprotein are less stable to hydrochloric acid than the phosphoproteins, inorganic phosphoric acid being eliminated from them during the course of several days, whereas no inorganic phosphoric acid is separated from the phosphoproteins.

III. Separation of Phosphorus from Glycerophosphoric Acid and Lecithin.

Besides nucleoprotein and phosphoprotein (or nuclealbumin), two other phosphorus-containing substances are found in all tissues, namely,

glycerophosphoric acid and lecithin. Glycerophosphoric acid is generally obtained by boiling lecithin with baryta. The separation of phosphoric acid from them by one per cent. sodium hydroxide at 37° would therefore not be expected, but it was essential for the purpose of determining the presence of phosphoprotein in the tissues to make quite certain of the stability of these substances.

Experiment 1.—Five c.c. of glycerophosphoric acid (Merck) were treated with 180 c.c. of one per cent. sodium hydroxide at 37° . Samples of 10 c.c. were removed at intervals, and the inorganic P_2O_5 was estimated as magnesium pyrophosphate. Total P_2O_5 by Neumann's modified method.

Experiment 2.—Five c.c. of glycerophosphoric acid (Merck) were treated with 175 c.c. of one per cent. hydrochloric acid at 37° . Samples of 10 c.c. were removed at intervals, and tested for inorganic P_2O_5 as above. Total P_2O_5 by Neumann's modified method.

EXPERIMENT I.		EXPERIMENT II.	
Time.	Inorganic P_2O_5 . (milligrams).	Time.	Inorganic P_2O_5 (milligrams).
0	1.0	0	1.3
18 hours	0.9	18 hours	1.0
24 „	0.9	24 „	0.8
4 days	1.0	4 days	1.3
107 „	11.8*	107 „	1.9
Total	24.8	Total	81.1

The solution of glycerophosphoric acid thus contained a minute quantity of inorganic phosphoric acid at the commencement, but this did not increase in amount.

The lecithin employed in these experiments was prepared from egg-yolks by extracting with ether, evaporating the solvent, and dissolving out the lecithin contained in the extract by means of alcohol. The alcoholic solution was concentrated to a volume of 400 c.c.

Experiment 1.—Two hundred c.c. of lecithin solution were mixed with 200 c.c. of 2 per cent. sodium hydroxide and kept at 37° . Samples of 50 c.c. were withdrawn at intervals, and precipitated by one c.c. of glacial acetic acid. Fifty c.c. of water were then added to facilitate filtration. Soluble P_2O_5 and inorganic P_2O_5 were estimated by the usual method. No determinations could be made with the first sample, as it was impossible to filter it clear. Total P_2O_5 was estimated in a special sample of 5 c.c.

Experiment 2.—Two hundred c.c. of lecithin were mixed with 15 c.c. of concentrated hydrochloric acid in 200 c.c. of water (= 2 per cent. HCl). Samples were withdrawn at intervals and filtered. The filtrate

* The precipitate was probably silica, due to the action of the soda on the glass vessel; the solution at the same time contained flakes of silica, but was filtered before testing for inorganic P_2O_5 .

always contained fatty acid, so that no determinations of inorganic P_2O_5 could be made. The filtrate was tested by the reagent employed by Scott for detecting phosphates in tissues (*J. Physiol.*, 1906, 35, 119).

EXPERIMENT I.			EXPERIMENT II.		
Time.	Soluble P_2O_5 (milligrams).	Inorganic P_2O_5	Time.	Soluble P_2O_5 (milligrams).	Inorganic P_2O_5
0	—	—	0	—	0
6 hours	97.3	0	6 hours	—	0
24 "	97.3	0	24 "	—	0
48 "	93.5	0	48 "	—	0
5 days	94.8	0	5 days	—	0
11 "	—	0	11 "	—	0
Total ...	97.6		Total ...	98.9	

No inorganic phosphoric acid is thus formed from these compounds under the above conditions. The stability of the phosphorus in them is therefore considerable; even boiling with 2*N*-nitric acid for one and a-half hours does not separate inorganic phosphoric acid from lecithin; the presence of inorganic phosphoric acid was observed only after five hours.

IV. Action of One per cent. Sodium Hydroxide on Tissues.

Having thus found that the phosphoproteins alone amongst the phosphorus-containing compounds in the animal body are acted on by one per cent. sodium hydroxide in such a way that their phosphorus is eliminated as inorganic phosphoric acid in twenty-four hours at 37°, it was possible to employ this reaction as a means of detecting phosphoproteins in the various tissues of the body, and verifying the statements to be found in all the text-books on physiological chemistry, that nuclealbumins (now phosphoproteins) are very widely distributed in the animal organism and are present in almost all cells. The evidence on which these statements are based appears to be due simply to the presence of phosphorus in substances prepared from extracts of tissues, and from the fact that no purine bases have been obtained from them by hydrolysis with acids. The formation of purine bases by hydrolysis is at present the only means of distinguishing between nucleoproteins and phosphoproteins. The separation of the purine bases is a matter of considerable difficulty, but they can be tested for by precipitation with silver nitrate in ammoniacal solution. Further, it is very doubtful whether all the substances described as nuclealbumins* have been tested for nucleoprotein by this method, and whether the inorganic phosphates present in all tissues have been excluded.

* Many of the substances described as nuclealbumins are undoubtedly nucleoproteins.

A. *Egg yolk*.—Before examining the tissues, it was advisable to ascertain the action of one per cent. sodium hydroxide on egg-yolks, which contain both lecithin and phosphoprotein with a small amount of nucleoprotein. No inorganic phosphates are present in egg-yolks, and they thus differ from tissues which contain in addition a greater proportion of nucleic acid and nucleoprotein.

Experiment 1.—Three egg-yolks weighing 50 grams were mixed with 500 c.c. of one per cent. sodium hydroxide and kept at 37°. Samples of 100 c.c. were withdrawn at intervals and precipitated by 2 c.c. of glacial acetic acid. Soluble P_2O_5 was estimated in a known volume of the filtrate by Neumann's modified method, and inorganic P_2O_5 as magnesium pyrophosphate by precipitation with ammonium magnesium citrate. The total P_2O_5 in the solution was estimated in a special sample of 10 c.c. All values are calculated for a sample of 100 c.c.

Experiment 2.—Three egg-yolks weighing 48 grams were treated with 500 c.c. of one per cent. sodium hydroxide at the ordinary temperature. Samples of 100 c.c. were withdrawn and treated as in experiment 1. Values calculated for 100 c.c. samples.

EXPERIMENT I.			EXPERIMENT II.		
Time.	Soluble P_2O_5 (milligrams).	Inorganic P_2O_5 (milligrams).	Time.	Soluble P_2O_5 (milligrams).	Inorganic P_2O_5 (milligrams).
0	9.1	5.2	0	9.1	4.9
5 hours	69.2	16.7	5 hours	40.5	10.0
22 "	109.3	28.2	22 "	81.6	15.0
30 "	110.6	33.1	30 "	90.3	16.6
48 "	113.2	33.7	48 "	97.3	19.8
Total ...	121.7		Total ...	120.5	

Inorganic phosphoric acid is thus completely separated from egg-yolk by one per cent. sodium hydroxide at 37° in about thirty hours; at the ordinary temperature, the separation is not complete in this time. There is a distinct increase of inorganic phosphate noticeable between 0, 5, and 22 hours, and also 30 hours, but at this stage it is not so marked. The amount of inorganic phosphate is about one-third the amount of soluble P_2O_5 in experiment 1, and about one-fifth in experiment 2.

B. *Pancreas (Ox)*. *Experiment 3*.—Three hundred and forty-five grams of minced material were thoroughly mixed with 1000 c.c. of one per cent. sodium hydroxide and kept at 37°. A somewhat gelatinous solution resulted, and the first sample was difficult to obtain on account of lumps. Samples of 100 c.c. were withdrawn at intervals and precipitated by 2 c.c. of glacial acetic acid. Soluble P_2O_5 and inorganic P_2O_5 were estimated in the filtrate by the usual methods.

Values calculated for 50 c.c. sample. The results are tabulated below.

C. *Lymphatic Glands (Ox)*. *Experiment 4*.—Ninety-three grams of minced material were treated with 500 c.c. of one per cent. sodium hydroxide at 37°. Samples of 100 c.c. were taken at intervals and treated as described under B.

D. *Thymus (Ox)*. *Experiment 5*.—One hundred and forty grams of minced gland were treated with 1000 c.c. of one per cent. sodium hydroxide at 37°. Samples of 100 c.c. were taken and treated as under B.

Experiment 6.—Sixty grams of minced thymus were treated with 1000 c.c. of one per cent. sodium hydroxide at 37°. Samples of 100 c.c. were removed and examined as under B.

E. *Liver (Dog)*. *Experiment 7*.—Two hundred and twenty-one grams of minced liver were mixed with 500 c.c. of one per cent. sodium hydroxide and kept at 37°. Samples of 100 c.c. were taken at intervals and acidified with 2 c.c. of glacial acetic acid. Soluble P_2O_5 and inorganic P_2O_5 were estimated in the filtrate as under B.

F. *Kidney (Dog)*. *Experiment 8*.—Thirty-nine grams of minced material and 350 c.c. of one per cent. sodium hydroxide were kept at 37°. Samples of 100 c.c. were taken and treated as under B.

G. *Testis (Ox)*. *Experiment 9*.—Five hundred and twenty grams of minced testis were mixed with 1000 c.c. of water. Seventy-five c.c. were removed and acidified. Soluble P_2O_5 and inorganic P_2O_5 were estimated in the filtrate and calculated for 50 c.c. sample. The values were 33.0 milligrams of soluble P_2O_5 and 17.9 milligrams of inorganic P_2O_5 . To remainder of mixture, 500 c.c. of *N*-sodium hydroxide were added; alkalinity = one per cent. Samples of 150 c.c. were removed and precipitated by 3 c.c. of glacial acetic acid. Soluble P_2O_5 , inorganic P_2O_5 , and also soluble *N*, by Kjeldahl's method, were estimated in the filtrate and calculated for 50 c.c. sample. The results are given below.

Experiment 10.—Two hundred c.c. of minced testis were squeezed through cloth to remove lumps, and then mixed with 400 c.c. of water and 200 c.c. of 10 per cent. sodium hydroxide; alkalinity = 2 per cent. Samples of 100 c.c. were removed and precipitated by 5 c.c. of glacial acetic acid. Soluble P_2O_5 , inorganic P_2O_5 , and soluble *N*, by Kjeldahl's method, were estimated in filtrate. All values calculated for 50 c.c. sample.

B. *Pancreas*, EXPERIMENT III.

Time.	Soluble P_2O_5 (milligrams).	Inorganic P_2O_5 (milligrams).
0	27.2	11.4
17 hours	111.5	18.1
24 "	115.7	18.2
41 "	117.7	18.4
48 "	119.7	18.4
65 "	118.3	19.9
3 days	117.1	17.6
4 "	120.3	21.7
16 "	—	20.3
119 "	130.6	23.6
Total ...	128.7	

C. *Lymphatic Glands*, EXPERIMENT IV.

Time.	Soluble P_2O_5 (milligrams).	Inorganic P_2O_5 (milligrams).
0	9.7	7.3
18 hours	31.4	12.7
24 "	30.1	12.9
41 "	32.9	12.5
48 "	33.3	13.1
7 days	40.8	20.2
Total ...	52.6	

D. *Thymus*, EXPERIMENT V.

Time.	Soluble P_2O_5 (milligrams).	Inorganic P_2O_5 (milligrams).
0	19.7	5.0
7 hours	22.3	10.4
24 "	25.5	10.2
31 "	25.5	10.9
48 "	23.9	10.1
55 "	27.2	11.2
3 days	27.5	10.4
4 "	23.4	10.2
10 "	27.5	10.9
Total ...	65.9	

D. *Thymus*, EXPERIMENT VI.

Time.	Soluble P_2O_5 (milligrams).	Inorganic P_2O_5 (milligrams).
0	6.1	2.9
7 hours	9.4	5.8
24 "	13.6	4.1
31 "	14.9	5.5
48 "	13.9	5.9
55 "	13.9	5.6
3 days	13.9	5.3
4 "	15.2	5.3
10 "	15.2	4.5
Total ...	34.2	

E. *Liver*, EXPERIMENT VII.

Time.	Soluble P_2O_5 (milligrams).	Inorganic P_2O_5 (milligrams).
0	22.0	11.9
18 hours	73.1	16.8
24 "	78.3	17.5
42 "	84.7	17.7
48 "	82.8	19.1
5 days	87.9	18.5
Total ...	88.8	

F. *Kidney*, EXPERIMENT VIII.

Time.	Soluble P_2O_5 (milligrams).	Inorganic P_2O_5 (milligrams).
0	3.6	2.6
18 hours	21.0	6.1
24 "	19.4	6.2
5 days	19.0	7.4
Total ...	26.6	

G. *Testis*, EXPERIMENT IX.

Time.	Soluble P_2O_5 (milli- grams).	Inorganic P_2O_5 (milli- grams).	Soluble N (gram).
0	31.0	15.7	0.0450
18 hours	53.3	17.9	0.1014
24 "	52.1	18.4	0.1071
48 "	53.1	17.9	0.1249
3 days	52.1	19.2	0.1342
19 "	52.7	17.7	0.1585
26 "	58.8	18.2	0.1913
44 "	58.2	18.9	0.1963
168 "	62.4	22.7	—
Total ...	66.6		0.2072

G. *Testis*, EXPERIMENT X.

Time.	Soluble P_2O_5 (milli- grams).	Inorganic P_2O_5 (milli- grams).	Soluble N (gram).
0	33.6	17.0	0.1036
20 hours	58.6	19.3	0.1113
26 "	57.9	18.7	0.1176
48 "	60.2	18.8	0.1271
70 "	60.9	20.3	0.1344
5 days	60.6	19.3	0.1463
10 "	61.6	20.2	0.1603
Total ...	68.5		0.3682

In the case of these tissues, it is seen that the soluble P_2O_5 increases very rapidly during the first twenty-four hours and then remains almost constant. A well-marked rise also occurs in the amount of the inorganic phosphoric acid between the first and second samples. There is no progressive rise in its amount as is observed in the case of egg-yolk. This rise might be taken to indicate the presence of phosphoprotein in the organs, but it is really due to the presence of inorganic phosphates in the tissues, which are only completely liberated when the tissue has passed into solution, a process which requires the same length of time; no increase is noticeable in its amount between the periods of seven hours or eighteen hours and twenty-four hours, as would be expected if phosphoprotein were present. The smallest increase is noticeable in the experiments with testis; here the organ, after mincing, consists of a thin cream containing only small lumps, and in the second experiment, the lumps were removed by straining through a cloth. Further, an attempt made to estimate the amount of inorganic phosphate before the tissue was treated with alkali indicates that the quantity of phosphate before and after the action of alkali for twenty hours was the same. A similar rise occurs if the organ is treated with 5 per cent. sulphuric acid, which does not act on phosphoproteins, as the following experiment (1) shows.

1. Four hundred and ninety grams of testis and 2000 c.c. of approximately *N*-sulphuric acid were incubated at 37° . Samples of 50 c.c. were removed and precipitated by 50 c.c. of tannic acid. Soluble P_2O_5 was estimated in the filtrate by Neumann's modified method. At the same time, a portion of the mixture was filtered, and 50 c.c. precipitated by ammonium magnesium citrate for inorganic P_2O_5 . Total P_2O_5 was estimated in a special sample of 10 c.c. All values calculated for 50 c.c. sample.

In another experiment (2), the complete precipitation of inorganic phosphates in the presence of organic matter was specially tested for; as previously found by Plimmer and Bayliss, and frequently verified during the course of these experiments, the presence of organic matter does not inhibit its complete precipitation.

Three hundred and twenty grams of testis and a 1000 c.c. of 2*N*-hydrochloric acid were kept at 37° . Samples taken as before. Inorganic P_2O_5 , however, was only estimated at three-day and eight-day intervals, but here 10 c.c. of potassium dihydrogen phosphate were also added to show that complete precipitation occurred:

50 c.c. gave 0.6278 gram $Mg_2P_2O_7$	} Mean = 0.0272 gram $Mg_2P_2O_7$ = 17.4 milligrams P_2O_5
50 c.c. + 10 c.c. KH_2PO_4 gave 0.6386	
gram $Mg_2P_2O_7$	
10 c.c. KH_2PO_4 gave 0.0320	
gram $Mg_2P_2O_7$	Diff. = 0.0266

50 c.c. gave 0.0298 gram $Mg_2P_2O_7$	} Diff. = 0.0292	} Mean = 0.0295 gram $Mg_2P_2O_7$ = 18.9 milligrams P_2O_5
50 c.c. + 10 c.c. KH_2PO_4 gave 0.0612		
gram $Mg_2P_2O_7$		
10 c.c. KH_2PO_4 gave 0.0320		
gram $Mg_2P_2O_7$		

EXPERIMENT I.

Time.	Soluble P_2O_5 (milligrams).	Inorganic P_2O_5 (milligrams).
0	13.2	5.1
16 hours	33.5	6.9
40 "	40.8	11.0
48 "	43.4	10.6
3 days	43.4	—
4 "	49.2	—
5 "	50.0	—
7 "	50.0	12.4
Total.....	55.8	

EXPERIMENT II.

Time.	Soluble P_2O_5 (milligrams).	Inorganic P_2O_5 (milligrams).
0	20.0	—
16 hours	50.5	—
24 "	55.0	—
48 "	59.3	—
3 days	61.2	17.4
4 "	62.1	—
8 "	64.2	18.9
Total.....	67.2	

We may conclude, therefore, that phosphoproteins are not present in the above tissues.

In addition to the supposed presence of phosphoproteins in the above tissues, the substances known as ichthulin, ichthin (Hammarsten, *Lehrbuch der physiologischen Chemie*), etc., prepared from the eggs of fishes, are regarded as phosphoproteins, as they contain a considerable amount of phosphorus and are usually obtained in the manner employed for preparing vitellin. It was therefore desirable to examine the behaviour of these organs towards one per cent. sodium hydroxide. The following experiments have been performed:

Experiment 1.—Three herring ovaries (67 grams) were treated with 850 c.c. of one per cent. sodium hydroxide at 37° . Samples of 100 c.c. were removed and precipitated by 2 c.c. of glacial acetic acid. Soluble P_2O_5 and inorganic P_2O_5 were estimated in the filtrate. Values calculated for 50 c.c. sample.

Experiment 2.—Four herring ovaries (93 grams) were mixed with 1700 c.c. of one per cent. sodium hydroxide. Samples removed as in experiment 1.

Experiment 3.—Three mackerel ovaries (56 grams) were treated with 1000 c.c. of one per cent. sodium hydroxide at 37° . Samples removed as in experiment 1.

Experiment 4.—Two hundred and thirty grams of cods' ovaries were mixed with 600 c.c. of one per cent. sodium hydroxide, and kept at 37° . Samples removed as in experiment 1.

Experiment 5.—One hundred and twenty-two grams of cods' ovaries were treated with 350 c.c. of one per cent. hydrochloric acid at 37° . Samples removed and filtered. Soluble P_2O_5 and inorganic P_2O_5 were

estimated in filtrate in the usual way. All values calculated for 50 c.c. sample.

EXPERIMENT I.			EXPERIMENT II.		
Time.	Soluble P_2O_5 (milligrams).	Inorganic P_2O_5 (milligrams).	Time.	Soluble P_2O_5 (milligrams).	Inorganic P_2O_5 (milligrams).
0	13.7	7.6	0	10.7	5.3
17 hours	37.2	14.9	17 hours	28.1	11.3
24 "	33.2	15.1	24 "	29.1	11.2
41 "	38.2	15.4	41 "	29.1	11.1
49 "	37.2	14.5	49 "	28.4	11.2
3 days	36.9	14.8	3 days	29.7	11.1
7 "	36.2	14.9	7 "	28.4	11.5
Total.....	39.3		Total.. ...	31.1	

EXPERIMENT III.			EXPERIMENT IV.		
Time.	Soluble P_2O_5 (milligrams).	Inorganic P_2O_5 (milligrams).	Time.	Soluble P_2O_5 (milligrams).	Inorganic P_2O_5 (milligrams).
0	14.7	8.5	0	29.8	18.7
3 hours	25.1	10.1	3 hours	30.8	20.1
20 "	32.3	15.0	17 "	73.7	26.3
24 "	32.8	16.6	24 "	75.0	26.9
28 "	32.3	16.5	43 "	78.9	29.2
44 "	—	16.8	3 days	80.3	31.5
51 "	—	16.2	5 "	80.8	—
3 days	32.3	16.7	8 "	82.1	34.1
Total.....	34.9		Total.....	79.9	

EXPERIMENT V.		
Time.	Soluble P_2O_5 (milligrams).	Inorganic P_2O_5 (milligrams).
0	31.7	17.6
17 hours	43.1	18.0
49 "	48.8	11.9
5 days	57.7	—
Total.....	74.3	

Just as in the case of the tissues, the results with the ovaries of fishes seem to indicate the presence of phosphoprotein; there is an increase of inorganic P_2O_5 as well as an increase of soluble P_2O_5 , which is very small in comparison. It is scarcely sufficient to demonstrate the presence or absence of phosphoprotein in the ovaries, the marked increase occurring at a period of about seventeen hours. For further proof of the presence of phosphoprotein, preparations were made from the ovary of the mackerel and of the cod by grinding the organs with sand, extracting them with 10 per cent. sodium chloride, precipitating with water, and repeating the process once more. Lecithin was removed by boiling with alcohol and ether. The preparation from mackerel ovaries showed only a trace of phosphorus, but that from cod contained 0.61 per cent. 3.5 Grams of this preparation were treated

with 350 c.c. of one per cent. sodium hydroxide at 37°, with following result :

Time	Soluble P_2O_5 (milligrams).	Inorganic P_2O_5 (milligrams).
0	trace	1.3 ?
6 hours	3.9	—
24 "	3.2	2.9
48 "	3.9	3.9
3 days	3.9	5.2
6 "	3.9	3.9
Total.....	4.4	

Although the differences here are so small, a distinct increase in the amount of inorganic P_2O_5 is noticeable in the periods 0, 24, 48 hours, from which it may be concluded that phosphoprotein is present; further, the amount of inorganic P_2O_5 is nearly the same as the amount of the total P_2O_5 , which again points to the presence of phosphoprotein in ichthulin from cods' ovaries.

Sufficient evidence for actually deciding on the presence or absence of phosphoprotein, both in the organs of the animal body and in the ovaries of fishes, is not really given by the above results. Another method was therefore devised for this purpose, in which the amount of the various kinds of phosphorus compounds in the organs could also be estimated. It consists in coagulating the protein with alcohol, extracting the lecithin and fat from the coagulum with boiling alcohol and ether, dissolving out the inorganic phosphates with dilute acid, and then treating the coagulated protein, dried with alcohol and ether, with one per cent. sodium hydroxide for twenty-four to forty-eight hours. As carried out, the method is as follows :

A quantity of finely-minced tissue is weighed out in a beaker and mixed with alcohol. After standing for a few days so as to coagulate the protein, the mixture is heated on the water-bath to complete the coagulation, and poured into a linen bag suspended to three hooks in a cylindrical glass vessel about $2\frac{1}{2}$ inches in diameter and 10—12 inches long, which is drawn out at one end, and resembles a Hempel fractionating column without the side-tube. The alcohol is thus separated from the coagulated protein, from which the lecithin and fat is now thoroughly extracted with boiling alcohol and ether. This is effected by inserting the glass vessel containing the linen bag into an Erlenmeyer flask of 600 c.c. capacity, and attaching a condenser at the other end so that the drops of condensed vapour fall inside the bag, alcohol or ether being placed in the flask as required. The whole extraction thus occurs at about the boiling point of the solvent, and is complete after six to eight hours' extraction with both solvents.*

* A similar procedure has been adopted by Koch and Woods (*J. Biol. Chem.*, 905, 1, 295), who suspend a small Gooch crucible inside a flask just over the surface

The linen bag is next removed from the glass vessel, and placed in dilute hydrochloric acid (one per cent.) to dissolve out the inorganic phosphates; this is changed four or five times, the bag being pressed between each extraction in order to remove as much adherent liquid as possible. It is then placed in ten to twelve changes of water to remove the acid, and then in several changes of alcohol to remove the water. It is finally extracted as before with boiling alcohol and ether. The several extracts obtained by this procedure, namely: (1) original alcohol + water from the tissue, (2) alcohol, (3) ether, (4) acid, (5) water, (6) water + alcohol, (7) alcohol, (8) ether, are treated so that only an ethereal extract and an aqueous (+ acid) extract are obtained.

Extracts (1), (2), and (3) are evaporated to dryness, and the residue is extracted repeatedly with ether to dissolve the lecithin and fat. It is very important to evaporate completely to dryness, since these extracts contain, in addition to the fatty substances, other phosphorus compounds which are soluble in dilute alcohol (such as extract 1), but are insoluble in absolute alcohol or ether. The ether is poured off and filtered into a measuring flask (ether extract). The residue which is insoluble in ether, is treated with water; except for a small residue consisting of coagulated protein, this is easily soluble; on filtration, an aqueous extract is obtained, which is added to that obtained from (4) and (5). The insoluble residue, together with the filter-paper from which it cannot be separated, is treated with one per cent. sodium hydroxide (see below).

Extracts (4) and (5) generally contain a fine suspension of particles of coagulated protein, from which they are filtered. The filtrates constitute together the water extract. The insoluble residue, together with the filter-papers, is treated with one per cent. sodium hydroxide (see below).

Extract (6), if acid, is neutralised with ammonia and evaporated to dryness. Extracts (7) and (8) are also evaporated to dryness. The residues are treated with (a) ether and (b) water. These are filtered and added to the other ethereal and aqueous extracts. The residue is treated with one per cent. sodium hydroxide (see below).

The ethereal and aqueous extracts are then made up to a definite volume in measuring flasks. There remains the coagulated protein in the linen bag; this, together with the bag, is placed with about 400 c.c. of one per cent. sodium hydroxide in a 600 c.c. flask, the other sodium hydroxide solutions (above) are added, and the flask is placed in an incubator at 37° for twenty-four to forty-eight hours. At the end of this time, the protein has passed completely into solution, and of the boiling solvent. This only allows of the extraction of 10–15 grams of material. It cannot be conveniently used for the extraction of 50 or 100 grams of material, such as we have employed.

if phosphoprotein is present (see eggs below), its phosphorus is separated as inorganic phosphoric acid. It is allowed to cool, and the contents are separated from the bag and filter-papers and poured into a 1000 c.c. measuring flask; the bag and papers are washed with one per cent. sodium hydroxide, and the washings are added to the main bulk until the volume is exactly made up.

Phosphorus estimations are then made with aliquot portions of each of these solutions. These are (1) total P_2O_5 in the ethereal extract by Neumann's modified method; the pipettes employed here are washed with ether to remove the adhering fat; (2) total P_2O_5 by Neumann's modified method and inorganic P_2O_5 by precipitation as ammonium magnesium phosphate with ammonium magnesium citrate in the aqueous extract; (3) (a) total P_2O_5 in the alkaline solution by Neumann's modified method, and (b) inorganic P_2O_5 by precipitation as ammonium magnesium phosphate in the filtrate from a known volume acidified with acetic acid. Two determinations are made in each case, and the mean taken.

Several experiments were firstly carried out with eggs, in which the several varieties of phosphorus compounds, lecithin, nucleic acid, nucleoprotein, and phosphoprotein, occur. No inorganic phosphates are present in eggs,* and in this respect they differ from the tissues. The details of two of those experiments were:

Weight of contents of egg = 52.6 grams.			
Ethereal extract, 250 c.c.	25 c.c. contained 17.6252 mgm. P_2O_5 .		
	That is, in egg	176.2	mgm. P_2O_5
Aqueous extract, 1000 c.c.	100 c.c. contained 2.7262 mgm. P_2O_5 .		
	That is, in egg	27.3	" "
	100 c.c. contained no inorganic P_2O_5 .		
Alkali extract, 1000 c.c.	100 c.c. contained 8.342 mgm. P_2O_5 .		
	That is, in egg	83.4	" "
Total		286.9	mgm. P_2O_5
300 c.c. + 6 c.c. glacial acetic acid:	100 c.c. contained 7.74 mgm. inorganic P_2O_5 .		
	That is, in egg, 78.9 mgm. (=phosphoprotein).		
Weight of contents of egg = 51.5 grams.			
Ethereal extract, 250 c.c.	25 c.c. contained 18.5762 mgm. P_2O_5 .		
	That is, in egg	185.8	mgm. P_2O_5
Aqueous extract, 1000 c.c.	100 c.c. contained 2.2821 mgm. P_2O_5 .		
	That is, in egg	22.8	" "
	100 c.c. contained no inorganic P_2O_5 .		
Alkali extract, 1000 c.c.	100 c.c. contained 8.4322 mgm. P_2O_5 .		
	That is, in egg	84.3	" "
Total		292.9	mgm. P_2O_5
300 c.c. + 6 c.c. glacial acetic acid:	100 c.c. contained 6.2 mgm. inorganic P_2O_5 .		
	That is, in egg, 63.2 mgm. (=phosphoprotein).		

* Inorganic phosphates are formed during the development of the chicken, as we shall show in another communication.

From these figures, the percentages of the various kinds of phosphorus compounds in the egg can be calculated. They are respectively:

	Per cent.	Per cent.
Ether soluble P_2O_5 ("lecithin")	61.4	63.4
Water soluble P_2O_5 (nucleic acid + inorganic, if present)	9.5	7.8
Inorganic P_2O_5	0.0	0.0
Protein P_2O_5 (phosphoprotein + nucleoprotein) ...	29.1	28.8
Phosphoprotein P_2O_5	27.5	21.6

The phosphorus compounds soluble in ether thus make up some 60 per cent. of the total; nucleic acid and nucleoprotein in the water and alkali make up some 10–15 per cent., and phosphoprotein nearly 30 per cent.

The following experiments were carried out with tissues.

A. *Testis of Ox.*

1. Weight of minced tissue = 118.6 grams.

Ethereal extract, 250 c.c. 10 c.c. contained 8.876 mgm. P_2O_5 .	
That is, in testis	221.9 mgm. P_2O_5
Aqueous extract, 2000 c.c. 100 c.c. contained 14.3284 mgm. P_2O_5 .	
That is, in testis	285.6 " "
100 c.c. contained 9.21 mgm. inorganic P_2O_5 .	
That is, in testis, 184.2 mgm. P_2O_5 .	
Alkali extract, 1000 c.c. 100 c.c. contained 15.0358 mgm. P_2O_5 .	
That is, in testis	150.4 " "
Total	638.9 mgm. P_2O_5
300 c.c. + 6 c.c. glacial acetic acid: 100 c.c. filtrate contained no inorganic P_2O_5 (no phosphoprotein).	

2. Weight of minced tissue = 134.0 grams.

Ethereal extract, 250 c.c. 10 c.c. contained 7.1642 mgm. P_2O_5 .	
That is, in testis	179.1 mgm. P_2O_5
Aqueous extract, 2000 c.c. 100 c.c. contained 17.6253 mgm. P_2O_5 .	
That is, in testis	352.5 " "
100 c.c. contained 12.22 mgm. inorganic P_2O_5 .	
That is, in testis, 244.4 mgm. P_2O_5 .	
Alkali extract, 1000 c.c. 100 c.c. contained 11.1584 mgm. P_2O_5 .	
That is, in testis	111.6 " "
Total	643.2 mgm. P_2O_5
300 c.c. + 6 c.c. glacial acetic acid: 100 c.c. filtrate contained no inorganic P_2O_5 (no phosphoprotein).	

From these figures the percentages are:

	Per cent.	Per cent.
Ether soluble P_2O_5 ("lecithin")	33.7	27.8
Water soluble P_2O_5 (nucleic acid + phosphates) ...	43.5	54.8
Inorganic P_2O_5	27.9	38.0
Protein P_2O_5 (nucleoprotein + phosphoprotein) ...	22.8	17.3
Phosphoprotein P_2O_5	0.0	0.0

About 30 per cent. of the total P_2O_5 is thus soluble in ether; about 50 per cent. is inorganic P_2O_5 , and from 30—40 per cent. is in the form of nucleic acid and nucleoprotein. There is no phosphoprotein.

B. *Thymus*.

1. Weight of minced tissue = 83.3 grams.

Ethereal extract, 1000 c.c.	50 c.c. contained 5.2622 mgm. P_2O_5 .	
	That is, in thymus	105.2 mgm. P_2O_5
Aqueous extract, 2000 c.c.	100 c.c. contained 15.1526 mgm. P_2O_5 .	
	That is, in thymus	303.0 " "
	100 c.c. contained 7.74 mgm. inorganic P_2O_5 .	
	That is, in thymus, 154.8 mgm. P_2O_5 .	
Alkali extract, 1000 c.c.	100 c.c. contained 32.5876 mgm. P_2O_5 .	
	That is, in thymus	825.9 " "
Total		734.1 mgm. P_2O_5
300 c.c. + 6 c.c. glacial acetic acid: 100 c.c. filtrate contained no inorganic P_2O_5 (no phosphoprotein).		

2. Weight of minced tissue = 60.2 grams.

Ethereal extract, 500 c.c.	25 c.c. contained 3.2968 mgm. P_2O_5 .	
	That is, in thymus	65.9 mgm. P_2O_5
Aqueous extract, 2000 c.c.	100 c.c. contained 12.5532 mgm. P_2O_5 .	
	That is, in thymus	251.1 " "
	100 c.c. contained 5.05 mgm. inorganic P_2O_5 .	
	That is, in thymus, 101.0 mgm. P_2O_5 .	
Alkali extract, 1000 c.c.	100 c.c. contained 18.1324 mgm. P_2O_5 .	
	That is, in thymus	181.3 " "
Total		498.3 mgm. P_2O_5
300 c.c. + 6 c.c. glacial acetic acid: 100 c.c. filtrate contained no inorganic P_2O_5 (no phosphoprotein).		

Hence the percentages are:

	Per cent. (1).	Per cent. (2).
Ether soluble P_2O_5 ("lecithin")	14.3	13.2
Water soluble P_2O_5 (nucleic acid + phosphates) ..	41.3	50.4
Inorganic P_2O_5	21.1	20.3
Protein P_2O_5 (nucleoprotein + phosphoprotein)...	44.4	36.4
Phosphoprotein P_2O_5	0.0	0.0

About 20 per cent. is inorganic phosphate, 14 per cent. lecithin, and about 60 per cent. nucleic acid and nucleoprotein. No phosphoprotein is present.

C. Pancreas.

1. Weight of minced tissue = 107 grams.

Ethereal extract, 250 c.c.	10 c.c. contained 4.8184 mgm. P_2O_5 .	
	That is, in pancreas.....	129.5 mgm. P_2O_5
Aqueous extract, 1500 c.c.	75 c.c. contained 22.7606 mgm. P_2O_5 .	
	That is, in pancreas.....	455.2 " "
	150 c.c. contained 24.11 mgm. inorganic P_2O_5 .	
	That is, in pancreas, 241.1 mgm.	
Alkali extract, 1000 c.c.	50 c.c. contained 33.5848 mgm. P_2O_5 .	
	That is, in pancreas.....	471.7 " "
	Total	1047.4 mgm. P_2O_5
300 c.c. + 6 c.c. glacial acetic acid:	100 c.c. filtrate contained 3.2 mgm. inorganic P_2O_5 (phosphoprotein).	That is, in pancreas, 32.6 mgm.

2. Weight of minced tissue = 88.5 grams.

Ethereal extract, 500 c.c.	25 c.c. contained 3.7406 mgm. P_2O_5 .	
	That is, in pancreas	74.8 mgm. P_2O_5
Aqueous extract, 1500 c.c.	75 c.c. contained 17.5618 mgm. P_2O_5 .	
	That is, in pancreas.. ..	351.2 " "
As this solution gave a precipitate with ammonia, the inorganic P_2O_5 was estimated in the filtrate from this, thus 300 c.c. + 25 c.c. NH_4OH ; 150 c.c. filtrate contained 17.27 mgm. P_2O_5 .		
	That is, in pancreas, 187.1 mgm.	
Alkali extract, 1000 c.c.	50 c.c. contained 18.6396 mgm. P_2O_5 .	
	That is, in pancreas.....	372.8 " "
	Total	798.8 mgm. P_2O_5
300 c.c. + 6 c.c. glacial acetic acid:	100 c.c. filtrate contained 2.7 mgm. inorganic P_2O_5 (phosphoprotein).	That is, in pancreas 27.54 mgm.

Hence the percentages are:

	Per cent. (1).	Per cent. (2).
Ether soluble P_2O_5 ("lecithin")	11.5	9.4
Water soluble P_2O_5 (nucleic acid + inorganic) ...	43.5	44.0
Inorganic P_2O_5	23.0	23.4
Protein P_2O_5 (nucleoprotein + phosphoprotein) ...	45.0	46.6
Phosphoprotein P_2O_5	3.1	3.4

The pancreas thus contains about 3 per cent. of its phosphorus in the form of phosphoprotein. It will be interesting to determine how far the phosphoprotein in this gland is connected with its secretory function.

The three tissues examined differ markedly from the eggs; in the latter, the major part of the phosphorus is in the form of lecithin, and in the former, in the form of nucleic acid. The amount of inorganic phosphoric acid is about 20 per cent. of the total phosphorus, but rather more in the testis. It is possible that this represents the state of

activity of the tissue. It will be interesting to see whether other organs contain a small quantity of phosphoprotein, and especially whether the organs in which continual synthesis and decomposition is continually proceeding contain this substance.

These experiments have been extended to the ova of fishes, namely, to caviar, the ova of the sturgeon, to herrings' ova, and to the ova of the grey mullet; in one experiment only, with caviar, have complete estimations being carried out, since it is difficult to obtain these substances quite fresh for analysis; the caviar used was preserved with salt; the herring ova were smoked and preserved in oil; the mullet ova were dried in the sun and preserved in a casing of wax.

The following are the results of the experiments:

A. Caviar.

1. Weight of substance taken = 100.4 grams; this was extracted in the usual way with alcohol and ether; the eggs then appeared like seeds, and were very hard and tough; before extraction with water they were thoroughly pounded in a mortar, so as to break open the shell of keratin.

Ethereal extract, 500 c.c.	20 c.c. contained 10.7146 mgm. P_2O_5 .	
	That is, in caviar	267.9 mgm. P_2O_5
Aqueous extract, 1000 c.c.	100 c.c. contained 15.7232 mgm. P_2O_5 .	
	That is, in caviar	157.2 " "
	100 c.c. contained 9.21 mgm. inorganic P_2O_5 .	
	That is, in caviar, 92.1 mgm.	
Alkali extract, 1000 c.c.	50 c.c. contained 24.409 mgm. P_2O_5 .	
	That is, in caviar, 488.2 mgm. P_2O_5 .	
200 c.c. + 6 c.c. glacial acetic acid:	100 c.c. filtrate contained	
49.5 mgm. inorganic P_2O_5 (phosphoprotein).	That is, in caviar	504.9 " "
Total		930.0 mgm. P_2O_5

Hence the percentages are:

	Per cent.
Ether soluble P_2O_5 ("lecithin")	28.8
Water soluble P_2O_5 (nucleic acid + inorganic)	16.9
Inorganic P_2O_5	9.9
Protein P_2O_5 (nucleoprotein + phosphoprotein)	—
Phosphoprotein P_2O_5	54.3

2. Weight of substance = 69.3 grams. Extracted with alcohol and ether; then ground-up (weight = 23.3 grams) and extracted with water containing acid; extracted again with alcohol and ether, and residue treated with one per cent. sodium hydroxide for forty-eight hours.

Alkali extract, 500 c.c.	25 c.c. contained 17.4984 mgm. P_2O_5 .
	That is, in caviar, 350.0 mgm. P_2O_5 .
200 c.c. + 6 c.c. glacial acetic acid:	100 c.c. filtrate contained 69.78 mgm. inorganic
P_2O_5 (phosphoprotein).	That is, in caviar, 355.9 mgm.

B. Herring Ova.

1. Weight of substance = 66.1 grams. Extracted with alcohol and ether; then ground-up (weight = 21 grams), and extracted with water containing acid, alcohol, and ether; residue treated with one per cent. sodium hydroxide for forty-eight hours.

Alkali extract, 1000 c.c. 50 c.c. contained 3.2968 mgm. P_2O_5 .
That is, in herring ova, 65.94 mgm. P_2O_5 .

300 c.c. + 6 c.c. glacial acetic acid: 100 c.c. filtrate contained 7.1 mgm. inorganic P_2O_5 (phosphoprotein). That is, in herring ova, 72.4 mgm. P_2O_5 .

2. Weight of substance = 58.0 grams. Weight after extraction with alcohol and ether was 18.5 grams. Treated as above.

Alkali extract, 1000 c.c. 50 c.c. contained 2.6628 mgm. P_2O_5 .
That is, in herring ova, 53.3 mgm. P_2O_5 .

300 c.c. + 6 c.c. glacial acetic acid: 100 c.c. filtrate contained 5.5 mgm. inorganic P_2O_5 (phosphoprotein). That is, in herring ova, 56.1 mgm. P_2O_5 .

C. Mullet Ova.

1. Weight of substance = 41.9 grams. Extracted with alcohol and ether: weight 24.0 grams. Treated as above.

Alkali extract, 1000 c.c. 50 c.c. contained 6.4668 mgm. P_2O_5 .
That is, in mullet ova, 129.4 mgm. P_2O_5 .

300 c.c. + 6 c.c. glacial acetic acid: 100 c.c. filtrate contained 13.21 mgm. inorganic P_2O_5 (phosphoprotein). That is, in mullet ova, 135.05 mgm. P_2O_5 .

2. Weight of substance = 41.0 grams. Weight after extraction with alcohol and ether, 33.0 grams. Treated as above.

Alkali extract, 1000 c.c. 50 c.c. contained 8.1152 mgm. P_2O_5 .
That is, in mullet ova, 162.3 mgm. P_2O_5 .

300 c.c. + 6 c.c. glacial acetic acid: 100 c.c. filtrate contained 16.62 mgm. inorganic P_2O_5 (phosphoprotein). That is, in mullet ova, 169.5 mgm. P_2O_5 .

Phosphoprotein is therefore present in the ova of fishes, and of the total amount of protein phosphorus, practically the whole consists of phosphoprotein. Nucleoprotein no doubt also exists, but its amount could not be estimated, as the amount of phosphoprotein P_2O_5 found exceeded that of the total P_2O_5 . This is accounted for by the manner in which the samples were removed from the main solution; both contained particles of the insoluble keratin of the shell; in the estimation of the total P_2O_5 , these were included, but they were not included in the estimation of the inorganic P_2O_5 ; the 300 c.c. were acidified, and the filtrate, now free from particles, was employed. The differences are minute, and they do not signify, since the purpose of the experiments was to determine the presence or absence of phosphoprotein. It may be noted that the amount of phosphorus contained in the ichthulin from caviar exceeds 50 per cent. of the total phosphorus.

It may be concluded from the results of the experiments :

1. That phosphoproteins may be distinguished from nucleoproteins by the action of one per cent. sodium hydroxide at 37° for twenty-four to forty-eight hours ; the phosphorus is completely separated in this time as inorganic phosphoric acid.

2. That phosphoproteins are present in milk, egg-yolk, and in the ova of fishes, that is, in the substances which constitute the food-stuffs of the embryo bird and fish and the young mammal.

3. That a small quantity of phosphoprotein is present in the pancreas.

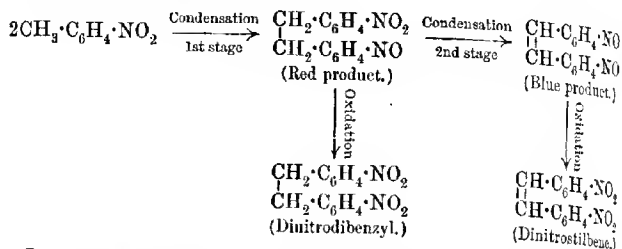
THE PHYSIOLOGICAL LABORATORY,
UNIVERSITY COLLEGE,
LONDON.

CLXVII.—*The Colouring Matters of the Stilbene Group.*
Part V. The Action of Caustic Alkalis on
Derivatives of para-Nitrotoluene.

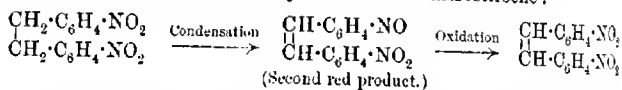
By ARTHUR GEORGE GREEN and JAMES BADDILEY.

In previous investigations conducted by one of the authors in conjunction with former collaborators (*Ber.*, 1897, 30, 3097; *Trans.*, 1904, 85, 1424, 1432; 1907, 91, 2076), it has been shown that the red, violet, or blue colorations, which mark the first stage of the action of caustic alkalis on *p*-nitrotoluene and its ortho-substituted derivatives, are due to the production of nitroso-compounds of stilbene and dibenzyl. These nitroso-compounds are too unstable to isolate as such, but were characterised by direct conversion into the corresponding nitro-compounds, the oxidation being effected either by means of air or hypochlorites. It was also shown that the readiness with which the nitroso-compound is produced depends on the electro-negativity of the ortho-substituting group, and, further, that those compounds (H , CH_3 , OMe , and CO_2H derivatives) which react least readily with alkalis give red colorations and, on oxidation, mainly derivatives of dinitrodibenzyl, whilst, on the other hand, those which react with alkalis most readily (Cl , CN , and SO_3Ph derivatives) produce blue colorations and, on oxidation, are converted more or less exclusively into derivatives of dinitrostilbene. The conclusion therefore seems justified that the red compounds represent nitronitrosodibenzyl derivatives (in the form of quinonoid salts), whilst the blue compounds are the dinitrostilbene derivatives (also as quinonoid salts), the rate of

conversion of the former into the latter being the factor which determines the ultimate formation of a dinitrodibenzyl or a dinitrostilbene compound when oxidation accompanies the condensation. These relationships may be expressed by the scheme:



In the technically-important instance of *p*-nitrotoluenesulphonic acid, Green and Wahl have shown that either the dibenzyl or the stilbene derivative can be obtained, according to the conditions of alkalinity and temperature selected. Also, from *p*-nitrotoluene itself, both compounds are formed. In these cases, therefore, it may be concluded that either the intermediate coloration represents a mixture of the two nitroso-compounds, in which one or the other may predominate according to the conditions employed, or that the dinitrodibenzyl formed by oxidation of the first compound can undergo a further condensation with caustic alkalis with formation of a nitro-nitrosostilbene, which is finally oxidised to dinitrostilbene:



The latter reaction can certainly occur, for it has been observed by Green and Wahl that dinitrodibenzylsulphonic acid behaves towards alkalis somewhat similarly to *p*-nitrotoluenesulphonic acid, giving first an intermediate red coloration and then, as final product, a mixture of dinitrostilbenedisulphonic acid with the dyestuff Stilbene Yellow 8G.

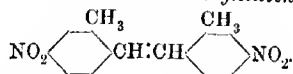
In the following experiments, we have endeavoured to ascertain in those cases in which hitherto only the formation of the dibenzyl compound was observed (the methyl, methoxyl, and carboxyl derivatives of *p*-nitrotoluene), whether a stilbene compound could be formed by carrying the reaction further. This was found to be the case, and dinitrodimethylstilbene, dinitrodimethoxystilbene, and dinitrostilbenedicarboxylic acid have thus been prepared.

We have also investigated the behaviour of 2:4-dinitrotoluene, which presents an extreme case of reactivity, giving excessively unstable, blue colorations even at temperatures far below zero, and even with such weak alkalis as sodium carbonate and ammonia. It

would therefore give rise exclusively to tetranitrostilbene, and this compound was, in fact, found to be the sole product. This example had not been previously studied, owing to the extreme instability of the intermediate nitroso-compound (rapid formation of brown condensation products), which rendered the previous methods of oxidation inapplicable. By employing an alkaline alcoholic solution of iodine as the oxidising agent, these difficulties have been overcome, and a nearly quantitative formation of tetranitrostilbene has been effected.

EXPERIMENTAL.

4 : 4'-Dinitro-2 : 2'-dimethylstilbene,



Five grams of finely-powdered *p*-nitro-*o*-xylene were mixed with 100 c.c. of cold methyl-alcoholic potash (33 per cent. KOH) in a 2-litre conical flask and vigorously shaken with air for one-half to three-quarters of an hour. As soon as the development of colour had nearly ceased, and a copious precipitate of dinitrodimethyldibenzyl was formed, the flask was heated on the water-bath and the reaction continued at a higher temperature. Colour formation again set in, and the vigorous agitation was continued in order to oxidise the nitroso-compound immediately it was formed. When the reaction again became sluggish, after about an hour at the higher temperature, the operation was stopped, the mixture cooled, the yellow precipitate quickly collected, and washed with hot alcohol and with water. A certain quantity of dinitrodimethyldibenzyl which it contained was removed by extraction with acetone, after which the product was recrystallised from nitrobenzene and pyridine, or, better, from tetrachloroethane.

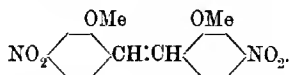
The substance forms yellow needles, which melt at 288–290° analysis gave :

Found: C = 64.10, 64.13; H = 4.35, 4.75; N = 9.23.

$\text{C}_{16}\text{H}_{14}\text{O}_4\text{N}_2$ requires C = 64.43; H = 4.7; N = 9.4 per cent.

The compound is sparingly soluble in solvents. It gives a crimson colour on reduction with phenylhydrazine in alkaline solution. The pyridine solution at once decolorises an acetone or a pyridine solution of calcium permanganate (distinction from dibenzyl derivative).

4 : 4'-Dinitro-2 : 2'-dimethoxystilbene,

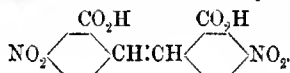


This compound was prepared in exactly the same way as the preceding one. It was readily obtained pure by two or three crystallisations from tetrachloroethane, in which solvent any accompanying dibenzyl derivative remains dissolved. The product forms bright orange needles, which melt at 268—269°. It gives the above-mentioned stilbene reactions with alkaline phenylhydrazine and with calcium permanganate. Analysis gave:

Found : C = 57.79, 58.29, 57.81 ; H = 4.0, 4.53, 3.87 ; N = 8.7, 8.4.

C₁₆H₁₄O₆N₂ requires C = 58.18 ; H = 4.24 ; N = 8.48 per cent.

4 : 4'-Dinitrostilbene-2 : 2'-dicarboxylic Acid,



Attempts to obtain this compound by air oxidation in the manner described above gave a product consisting of about equal parts of the stilbene acid and the previously-described dibenzyl acid. By employing sodium hypochlorite in large excess, better results were obtained. The best conditions were found to be the following: 10 grams of nitro-*o*-toluic acid were dissolved in 30 c.c. of 10 per cent. sodium carbonate solution. To this were added 100 c.c. of sodium hypochlorite solution (containing 9.4 per cent. of available chlorine) and 25 c.c. of sodium hydroxide solution (33 per cent.). The mixture was rapidly heated to boiling, and the reaction allowed to proceed spontaneously for three minutes, at the end of which time yellow crystals of sodium dinitrostilbenedicarboxylate began to separate. Directly the reaction slackened, and before the hypochlorite had quite disappeared, the whole mass was poured into dilute hydrochloric acid. The white precipitate of the free carboxylic acid was collected and washed. It was then dissolved in aqueous potassium carbonate, and the potassium salt recrystallised several times from water containing a little potassium carbonate. The free acid crystallises from cresol in small, pale yellow crystals, which melt with decomposition at 288—291°. Analysis gave:

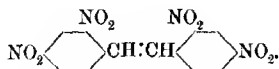
Found : C = 53.43, 53.37 ; H = 2.92, 2.87 ; N = 7.87.

C₁₆H₁₀O₈N₂ requires C = 53.63 ; H = 2.79 ; N = 7.82 per cent.

In alkaline solution, the acid gives a crimson colour with phenyl-

hydrazine, and decolorises cold dilute permanganate. The *potassium* salt forms yellow, pointed crystals. The *barium* salt is sparingly soluble, and forms large, needle-shaped crystals.

2 : 4 : 2' : 4'-Tetranitrostilbene,



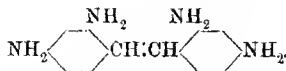
By acting on 2 : 4-dinitrotoluene with alcoholic potash in the cold, the blue nitroso-compound first formed rapidly undergoes further condensation to violet-brown, amorphous products before air has time to effect its oxidation. The following method of procedure, in which iodine was employed as the oxidising agent, gave excellent results : 20 grams of dinitrotoluene were dissolved in 50 c.c. of pyridine, and 32 grams of iodine dissolved in 220 c.c. of methyl alcohol were added. The mixture was cooled in a freezing mixture, and 70 c.c. of methyl-alcoholic potash (33 per cent.) were slowly added. As the potash was run in, the yellow colour of the iodine disappeared and the mixture became brown, eventually depositing a copious, crystalline precipitate. After standing half an hour, this was collected and washed with hot alcohol and with water. On drying, it formed a yellow, crystalline powder, which was nearly pure tetranitrostilbene. The yield was 15 grams. After crystallising twice from nitrobenzene, the product was obtained in pale yellow needles, which melted with decomposition at 264—266°. A nitrogen estimation gave :

Found : $N = 15.54$.

$C_{14}H_8O_8N_4$ requires $N = 15.55$ per cent.

The product is identical with the known tetranitrostilbene obtained by Krassusky (*J. Russ. Phys. Chem. Soc.*, 1895, 27, 335) from dinitrobenzyl chloride.

2 : 4 : 2' : 4'-Tetra-aminostilbene,



Tetranitrostilbene was reduced by boiling for several hours with tin and hydrochloric acid containing a little alcohol. The tin double chloride which separated was collected and converted into the hydrochloride by dissolving in a little water and precipitating with concentrated hydrochloric acid. After repeating this treatment two or three times, the hydrochloride was obtained free from tin in the form of greyish-white, crystalline needles, readily soluble in water, but

rather sparingly so in dilute hydrochloric acid. The free base was obtained in pale yellow leaflets by adding ammonia to the solution of the hydrochloride. It melts at 183—186°, and contains one molecule of water of crystallisation. A nitrogen estimation gave:

Found: N = 21.60, 21.62.

$C_{14}H_{16}N_4 \cdot H_2O$ requires N = 21.70 per cent.

Loss on heating to 100—110° for four hours:

Found: 6.71.

Loss of H_2O requires 6.97 per cent.

The compound is doubtless identical with the tetra-aminostilbene described by Echaes (*Ber.*, 1904, 37, 3599), who gives the melting point as being 191° or below.

The base is somewhat oxidisable. It is moderately soluble in water, and readily so in alcohol. On coupling with diazo-compounds, it gives rise to brown azo-dyestuffs.

DEPARTMENT OF TINCTORIAL CHEMISTRY,
THE UNIVERSITY, LEEDS.

CLXVIII.—*The Trithionates and Tetrathionates of the Alkali Metals. Part I.*

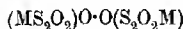
By JOHN EDWIN MACKENZIE (Research Fellow of the University of Edinburgh) and HUGH MARSHALL.

THE constitution and properties of the polythionates have been the subject of several papers recently published by various investigators, the principal being by A. Gutmann (*Ber.*, 1906, 38, 1728, 3277; 1907, 39, 509; 1907, 40, 3614; 1908, 41, 300, 1650), Julius Meyer and H. Eggeling (*Ber.*, 1907, 40, 1351), Price and Twiss (*Trans.*, 1907, 91, 2021), and Colefax (*Trans.*, 1908, 93, 811); the last-mentioned had previously published papers dealing with the same subject (*Trans.*, 1892, 61, 176, 199, 1083).

Some time ago, we commenced the fuller investigation of the reaction described by one of us (Marshall, *J. Soc. Chem. Ind.*, 1897, 16, 396), by means of which tetrathionate is produced by the interaction of persulphate and thio-sulphate. The investigation has occupied more time than we anticipated, and the completion of it may be delayed; we therefore have thought it advisable to communicate now the results which have already been obtained.

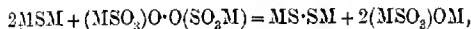
The Constitution of the Trithionates and Tetrathionates.

The constitutional formula for tetrathionates proposed by Mendeléeff has been assailed by Gutmann, who assigns to these salts a "peroxidic" in place of a "persulphidic" structure, thus :

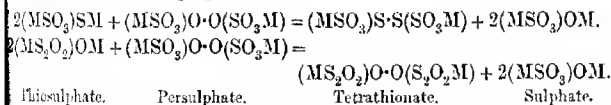


in place of $(\text{MSO}_3)\text{S}\cdot\text{S}(\text{SO}_3\text{M})$. It is unnecessary here to give a fuller statement of his views, seeing that a summary of them has already been given by Price and Twiss (*loc. cit.*). These authors show that certain results obtained by them are incompatible with Gutmann's assumption, which they reject in favour of the older view. In addition to the evidence which they bring forward, there are several other points which might be stated in favour of Mendeléeff's formula, and to which we desire to call attention.

In the first place, the occurrence of the reaction which has been referred to above as constituting the subject of the present investigation, would seem to contradict Gutmann's view. On the older assumption, the formation of tetrathionate in this action is quite analogous to the formation of persulphide along with sulphate by the interaction of sulphide and persulphate :



that is, the rupture of the peroxidic union in the persulphate is in each case associated with the formation of the much more easily effected persulphide union. On Gutmann's assumption, however, the rupture of the peroxidic union in the persulphate is associated with the formation of an exactly analogous peroxidic union in the tetrathionate, so that it is difficult to see why any such reaction should take place. The two views as to the nature of this reaction may be represented by means of the following equations :



Thiosulphate.

Persulphate.

Tetrathionate.

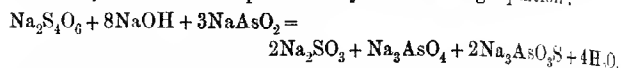
Sulphate.

Further, if Gutmann's view were correct, the formation of tetrathionate by the interaction of iodine and thiosulphate would be of a very exceptional character, since peroxidic union cannot generally be brought about by means of iodine, but, on the contrary, iodine is liberated from iodides by the action of peroxides or analogous compounds.

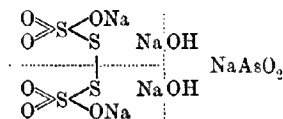
As stated by Price and Twiss, of the various reactions studied by Gutmann, only two have any direct bearing on the question of the constitution of tetrathionates ; the others are of too complex a nature

to afford evidence for or against either of the constitutional formulae under consideration.*

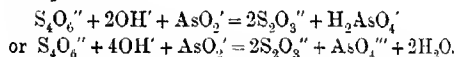
The first of these reactions is that of certain reducing agents, such as alkaline solution of arsenite, on tetrathionates. As observed by Gutmann, this action is represented by the following equation:



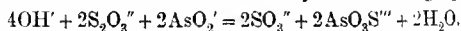
The striking point about the above reaction is the formation of arsenate in addition to monothioarsenate, seeing that it might have been expected that the function of the reagent in such a case would be to remove sulphur only. The fact that oxygen also is removed, forms the basis of Gutmann's argument for the peroxidic structure of the tetrathionate. The formation of arsenate can be explained very simply, however, without departing from the persulphide formula; it is only necessary to assume that the first action of the alkaline arsenite solution is, not to remove oxygen or sulphur from the tetrathionate, but to add sodium to it and so "reduce" it to thiosulphate, as illustrated in the following scheme:



or by the ionic equation:



But as Gutmann has shown, thiosulphate is acted on by an alkaline solution of arsenite with formation of sulphite and monothioarsenate. The complete action is therefore represented as taking place in two stages: the first as above, and the second by the following equation:

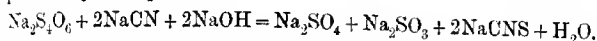


The following facts justify the above assumption as to the first action of the arsenite: (1) According to Spring (*Ber.*, 1874, 7, 1161), sodium amalgam acts on tetrathionate to produce thiosulphate. (2) If hydrochloric acid is added to a mixture of arsenate and iodide, arsenious chloride and iodine are produced, but in the presence of alkali (ar-

* In a number of cases, Gutmann's results are open to grave objection from the fact that, for these experiments, he did not prepare his solutions from pure tetrathionate, but used directly the solution obtained by adding an equivalent quantity of iodine to a solution of a thiosulphate. Our experiments have shown that the presence of small quantities of other substances often has a very great influence on the decomposition of tetrathionates, and the solutions used by Gutmann in these particular experiments would necessarily contain at least a slight excess of either iodine or thiosulphate.

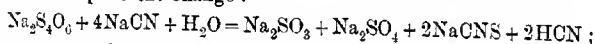
bonate), arsenite and iodine interact with formation of arsenate and iodide. Similarly, when hydrochloric acid is added to a mixture of arsenate and thiosulphate, arsenious chloride and tetrathionic acid are formed; it may therefore be surmised, in view of action (1), that probably here, also, the sense of the change will be reversed in presence of alkali, and that arsenite and alkali will form arsenate and thio sulphate.

The second reaction to be considered is that of alkaline cyanide solution on tetrathionate, which Gutmann shows to take place as expressed by the equation :



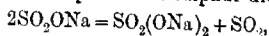
He, himself, makes no attempt to draw support for his formula from this reaction; as a matter of fact, his expectation was that the products would be sulphite, cyanate, and thiocyanate.

Gutmann states that the reaction takes place very slowly at the ordinary temperature, but this is not in accord with our experience. If a solution of tetrathionate is mixed with barium nitrate solution, and pure cyanide solution is added, the liquid remains clear only for a moment; a copious precipitation of barium sulphate and sulphite takes place almost instantaneously. The addition of alkali is not necessary, but if it is omitted, then twice as much cyanide has to be employed in order to complete the change :

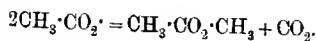


the presence of a great excess of hydrocyanic acid apparently does not affect the action.

In this case there is no need to assume the "reduction" of the tetrathionate to thiosulphate; the cyanide simply removes the two connecting sulphur atoms, leaving the two SO_3Na groups, which then interact with formation of sodium sulphate and sulphur dioxide, thus :



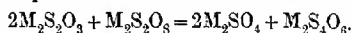
the sulphur dioxide would act either on the free alkali or, in its absence, on the cyanide, forming sodium sulphite. The formation of sulphate and sulphur dioxide from the two NaSO_3 groups would be to some extent analogous to one of the actions observed at the anode in certain electrolytic decompositions; for example, the formation of ethyl acetate from two $\text{CH}_3\cdot\text{CO}_2\cdot$ groups during the electrolysis of an acetate solution :



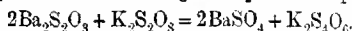
The difference in the action of the alkaline arsenite solution and of the alkaline cyanide solution on tetrathionate is therefore easily explicable, using the persulphide formula, and is due to the preliminary formation of thiosulphate in the first case and not in the other.

The Interaction of Thiosulphate and Persulphate.

This action, as has already been shown (Marshall, *loc. cit.*), is expressed by the equation:



In order to make use of this reaction as a means of preparing any particular tetrathionate, it is evident that a great advantage would be gained by using the thiosulphate of a metal which forms an insoluble sulphate along with the persulphate of the metal, the tetrathionate of which it is desired to obtain; in that case, if the proper proportions are employed, the resulting solution should contain the tetrathionate unmixed with other salt. In the first experiments, barium thiosulphate was used along with potassium persulphate:



Owing to the very sparing solubility of the barium salt, however, it was considered advisable to use, instead, the easily soluble strontium salt; this, notwithstanding its great solubility, can be obtained pure without much difficulty. The salt used for the experiments was prepared by fractional crystallisation from solutions of strontium nitrate and sodium thiosulphate. After three recrystallisations, the product gave, on analysis:

Sr = 30.39.

$Sr_2S_2O_3 \cdot 5H_2O$ requires Sr = 30.23 per cent.

A moderate quantity of the persulphates of rubidium and caesium being available, it was decided to make use of them for the preparation of the tetrathionates, seeing that these salts had not at that time been prepared. While the work was in progress, the paper by Meyer and Eggeling (*loc. cit.*) on the thiosulphates of these metals appeared. In it they described the preparation of the two tetrathionates by the action of iodine on the thiosulphates, the product being obtained from solution by the addition of alcohol. They thus obtained anhydrous, crystalline salts, which they analysed, but did not further describe. We had already obtained small quantities of hydrated crystals from purely aqueous solution, and saw no reason to discontinue our investigation.

The persulphates referred to above had been prepared by mixing a cold saturated solution of recrystallised ammonium persulphate with cold saturated solutions of rubidium chloride and caesium sulphate respectively. In each case a sparingly soluble salt is precipitated, containing, however, some ammonium salt in isomorphous mixture. In order to get rid of this impurity, the salt was in the first instance recrystallised as rapidly as possible from hot water, and subsequently

from hot water to which had been added a quantity of the appropriate hydroxide (or of barium hydroxide) sufficient to decompose the remaining ammonium persulphate.

Additional quantities of the salts had to be prepared later, and this was done either by the foregoing method or by double decomposition between ammonium persulphate and excess of the metallic hydroxide directly, in place of chloride or sulphate. When this method is employed, the ammonium salt must be added slowly to the hydroxide solution and not vice versa, otherwise the crystalline precipitate, which is first obtained, contains ammonium salt in isomorphous mixture.* The purified salts were analysed by conversion into the sulphate, and the results obtained in each case agreed closely with the numbers calculated for the anhydrous salt.

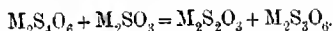
The reaction between persulphate and thiosulphate in solution takes place fairly rapidly, and is accompanied by considerable evolution of heat, so that to avoid decomposition due to rise of temperature, it is advisable to adopt some method of cooling the mixture. The method adopted was to place the materials in a long, narrow stoppered bottle, clamped to a wheel, which was rotated in a large vessel filled with cold water. It is desirable to avoid using excess of water to dissolve the reacting substances, since the somewhat unstable solution produced must subsequently be evaporated. In each case the quantity taken, whilst approximating to that required for the dissolution of the strontium thiosulphate, was not nearly sufficient to dissolve the persulphate, but was amply sufficient to retain in solution the tetrathionate produced. The precipitation of strontium sulphate may not begin until after the lapse of a minute or two, because of the increased solubility of the sulphate in presence of thiosulphate (compare Dobbin, *J. Soc. Chem. Ind.*, 1901, 20, 218).

After several hours' agitation, the bottle was removed and allowed to stand until the precipitate had completely settled. The clear liquid was then poured off through a Buchner filter, after which the precipitate was transferred to the filter, drained as completely as possible, and then washed twice with very small quantities of water. The dissolved salt may be separated from the solution either by precipitation with alcohol or by evaporation at the ordinary temperature.

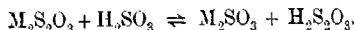
In the first experiments carried out in order to test the method, potassium persulphate was employed, and the tetrathionate was obtained without difficulty. When the method was next applied to the preparation of the rubidium salt, however, the yield of tetrathionate was not satisfactory. The solution behaved as if it were much less

* Commercial potassium persulphate, being prepared by double decomposition from the ammonium salt, contains small quantities of this salt; it can easily be purified in the above manner.

stable than that of the potassium salt; a considerable quantity of sulphur was deposited from it, and the crystals which were obtained consisted mainly of trithionate. As it appeared improbable that there should be a marked difference in the stability of the salts, the exact conditions of the two experiments were reviewed, and it was found that in the second experiment the thiosulphate was in slight excess of the theoretical proportion, whilst in the first it was somewhat deficient. Qualitative experiments were therefore made in order to find out if the decomposition of the tetrathionate might not be due to the presence of this slight excess of thiosulphate or its decomposition products (the solution becomes faintly acid). It was found that a pure solution of potassium tetrathionate at the ordinary temperature decomposes only slowly, with deposition of sulphur; the deposition of sulphur takes place more rapidly if a small quantity of thiosulphate, or of sulphurous acid, is added to the solution, and still more rapidly if both substances are added. The explanation of this is to be found in the observation made by Colefax (*loc. cit.*), that sulphite removes sulphur from tetrathionate with formation of thiosulphate and trithionate:



In a solution which, in addition to the above, contains free sulphurous acid, the action expressed in the following equation will take place:



This is not a stable equilibrium, however, since the sulphite will take up more sulphur from tetrathionate, and the thiosulphuric acid will decompose with deposition of sulphur and regeneration of sulphurous acid. The presence of thiosulphate and sulphurous acid together in the solution will therefore greatly accelerate the decomposition of tetrathionate in the direction of forming trithionate and liberating sulphur. In view of this fact, it is evident that a slight excess of per-sulphate must be used in the preparation of the tetrathionate. On the other hand, by using an excess of thiosulphate a satisfactory yield of trithionate may be obtained.

Before repeating the preparation of the tetrathionates of rubidium and caesium in larger quantity, we decided to complete the investigation of the trithionates, and additional quantities of these were prepared, seeing that no description of the preparation and properties of these salts has yet been given. For the sake of completeness, we also reexamined the potassium salt which has already been described.

Potassium Trithionate.

For the preparation of this salt, 20 grams of potassium persulphate, 46 grams of strontium thiosulphate (theoretically required: 42.4),

and 70 c.c. of water were employed. The filtered solution soon became milky, and a yellow deposit of sulphur mixed with strontium sulphate gradually formed; the liquid was allowed to evaporate spontaneously in a current of air, and was filtered each day.

By the time crystals began to form, the tetrathionate was nearly all decomposed, and the solution was then allowed to stand until the mother liquor was reduced to a small volume. This was then removed as completely as possible, the crystals dissolved in the minimum quantity of water at about 30°, and the resulting solution filtered and allowed to crystallise. This purification was repeated until the solution no longer deposited sulphur when allowed to stand for two or three hours.

For analysis, the sulphur was determined by oxidation with bromine and precipitation with barium chloride:

0.3038 gave 0.778 BaSO₄. S = 35.17.

K₂S₄O₆ requires S = 35.56 per cent.

By the above method, the salt was obtained in thin prisms, which were not suitable for crystallographic measurements. In order to obtain better crystals, a solution saturated at about 30° was allowed to cool very slowly by leaving it for four to five days in a large, double-walled cylinder, the annular space of this vessel being filled with water at the same temperature; the cylinder itself was embedded in a box of sawdust. In this way considerably larger prismatic crystals were obtained, some attaining as much as 50 mm. in length and 4 mm. in breadth. Few of the crystals were entirely clear throughout; the larger ones always exhibited elongated cavities in the interior.

The density of the crystals was determined on selected fragments by the method of free suspension in a dense liquid (mixture of tetrabromoethane and xylene), using the Westphal balance.

Seven determinations gave results varying from 2.3335 to 2.3395. Mean value: D = 2.336. This differs considerably from the values given by Hertlein (*Zeitsch. physikal. Chem.*, 1896, 19, 297), namely, 2.3044 and 2.3036. Probably Hertlein had not obtained sufficiently homogeneous material for his determinations. In order to make sure that our higher results were not due to the presence of some strontium compound, a quantity of the salt was prepared from potassium thio-sulphate and sulphur dioxide, and the density determined on fragments of crystals grown as above. The result obtained was the same as before. The above value gives a molecular volume of 115.8.

The geometrical crystallography of potassium trithionate has been studied by various investigators; de la Provostaye (*Ann. Chim. Phys.*, 1840, [iii], 3, 354), Rammelsberg (*Neueste Forschungen*, 1857, 27), and H. Baker (*Chem. News*, 1877, 36, 203) all describe the salt as forming

rhombic crystals which do not give very good measurements, owing to smallness or curvature of the faces; according to Rathke (*J. pr. Chem.*, 1870, [ii], 1, 35), the crystals are monoclinic, but he did not actually perform any measurements.

The data which we give were obtained with crystals grown as above mentioned:

System and class: Rhombic bipyramidal.

$$a:b:c=0.7168:1:0.4193.$$

Forms observed: $b=\{010\}$; $l=\{210\}$; $m=\{110\}$; $n=\{1\bar{2}0\}$, $q=\{011\}$.

FIG. 1.



In addition to these, the form $k=\{031\}$ was occasionally observed, but it is always small. de la Provostaye mentions a pyramidal face

Angle.	No. of observa- tions.	Limits.	Mean.	Calculated.
$l:l=210:210$	7	$39^{\circ}18' - 39^{\circ}47'$	$39^{\circ}26'$	*
$l:n=210:120$	11	$35^{\circ}17' - 35^{\circ}48'$	$35^{\circ}29'$	$35^{\circ}28'$
$l:m=210:110$	5	$15^{\circ}27' - 16^{\circ}0'$	$15^{\circ}42'$	$15^{\circ}56'$
$m:n=110:120$	6	$19^{\circ}36' - 20^{\circ}9'$	$19^{\circ}50'$	$19^{\circ}28'$
$n:b=120:010$	6	$34^{\circ}43' - 35^{\circ}2'$	$34^{\circ}53'$	$34^{\circ}54'$
$q:q=011:0\bar{1}1$	10	$45^{\circ}23' - 45^{\circ}36'$	$45^{\circ}30'$	*
$q:b=011:010$	10	$67^{\circ}11' - 67^{\circ}21'$	$67^{\circ}14'$	$67^{\circ}15'$
$q:k=011:031$	1	$25^{\circ}46'$	$28^{\circ}46'$	$28^{\circ}46'$
$k:b=031:010$	1	$38^{\circ}29'$	$33^{\circ}29'$	$38^{\circ}29'$
$q:l=011:210$	17	$82^{\circ}3' - 82^{\circ}45'$	$82^{\circ}25'$	$82^{\circ}30'$
$q:m=011:110$	8	$76^{\circ}49' - 77^{\circ}5'$	$76^{\circ}57'$	$76^{\circ}50'$
$q:n=011:120$	4	$71^{\circ}18' - 71^{\circ}27'$	$71^{\circ}26'$	$71^{\circ}30'$

$o = \{121\}$, but we did not observe this on any of our crystals. The faces of $\{011\}$ give very good reflections, but those of the vertical prisms are generally more or less curved and give poorer reflections; the faces $\{120\}$ are always narrow, and those of $\{010\}$ are frequently absent altogether.

No distinct cleavage.

When the crystals are examined through l in convergent polarised light, the interference figure seen indicates that the plane of the optic axes is parallel to $\{010\}$, with the axis c as acute bisectrix.

The refractive indices were determined by means of the total reflectometer, using the faces l and q . The values obtained are: $\alpha = 1.4925$, $\beta = 1.5646$, $\gamma = 1.6014$ (Na light).

The axial angle calculated from these gives the value:

$$2V = 68^\circ 15'.$$

Rubidium Trithionate.

The method for preparing and purifying this salt is similar to that described for the potassium compound, but with different proportions of material. Twenty grams of rubidium persulphate require theoretically only 31.9 grams of strontium thiosulphate; it is therefore advisable to take about 33 grams, along with 40—50 c.c. of water. Rubidium trithionate appears to be decidedly more soluble than the potassium salt, but forms more perfect crystals; those used for examination were obtained by slow cooling, as before, and the largest measured about 25 mm. by 3 mm.

For the analysis, the sulphur was determined as in the previous case, and the rubidium was also determined by direct conversion into sulphate:

0.2800 gave 0.5428 BaSO_4 . S = 26.63.

0.1831 „ 0.1811 Rb_2SO_4 . Rb = 47.0.

$\text{Rb}_2\text{S}_3\text{O}_6$ requires S = 26.52; Rb = 47.05 per cent.

The density, determined as before, was 2.845 as the average of seven determinations (limits, 2.843—2.847). Molecular volume = 127.7.

The crystals are isomorphous with the preceding salt, and are of a similar long-prismatic habit, although the forms observed are not all the same:

System and class: Rhombic bipyramidal.

$$a : b : c = 0.7058 : 1 : 0.4176.$$

Forms observed: $a = \{100\}$; $b = \{010\}$; $l = \{210\}$; $m = \{110\}$; $n = \{120\}$; $q = \{011\}$; $k = \{031\}$; $s = \{201\}$.

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In addition to these, the form $\sigma = \{111\}$ was also observed, but only on one crystal; it was not very small, however. The predominating forms are m , g , and s , the others being small and often incomplete.

Angle.	No. of observations.	Limits.	Mean.	Calculated.
$a : m = 100 : 110$	22	$34^{\circ}45' - 35^{\circ}25'$	$35^{\circ} 3'$	$35^{\circ} 13'$
$a : l = 100 : 210$	4	$19^{\circ}28' - 19^{\circ}38'$	$19^{\circ}33'$	$19^{\circ}26'$
$l : m = 210 : 110$	5	$15^{\circ}17' - 15^{\circ}59'$	$15^{\circ}44'$	$15^{\circ}46'$
$m : b = 110 : 010$	22	$54^{\circ} 5' - 55^{\circ}18'$	$54^{\circ}50'$	$54^{\circ}41'$
$m : n = 110 : 120$	7	$19^{\circ} 3' - 20^{\circ} 5'$	$19^{\circ}32'$	$19^{\circ}28'$
$n : b = 120 : 010$	6	$34^{\circ}52' - 35^{\circ}25'$	$35^{\circ}12'$	$35^{\circ}16'$
$b : g = 010 : 011$	2	$67^{\circ}21' - 67^{\circ}22'$	$67^{\circ}21'$	$67^{\circ}20'$
$b : k = 010 : 031$	12	$38^{\circ}24' - 38^{\circ}55'$	$38^{\circ}37'$	$38^{\circ}36'$
$k : g = 031 : 011$	19	$28^{\circ}35' - 28^{\circ}52'$	$28^{\circ}43'$	$28^{\circ}41'$
$g : q = 011 : 0\bar{1}1$	11	$45^{\circ} 9' - 45^{\circ}26'$	$45^{\circ}20'$	
$\sigma : s = 100 : 201$	11	$40^{\circ} 3' - 40^{\circ}23'$	$40^{\circ}12'$	$40^{\circ}12'$
$s : s' = 201 : 201$	9	$99^{\circ}28' - 99^{\circ}45'$	$99^{\circ}36'$	
$q : s = 011 : 201$	8	$53^{\circ}22' - 53^{\circ}30'$	$53^{\circ}26'$	$53^{\circ}26'$
$s : m = 201 : 110$	5	$51^{\circ} 7' - 51^{\circ}35'$	$51^{\circ}17'$	$51^{\circ}23'$
$\sigma' : q = 1\bar{1}0 : 011$	1	$90^{\circ} 4'$	$90^{\circ} 4'$	$90^{\circ} 0'$
$\sigma : o = 100 : 111$	1	$61^{\circ}22'$	$61^{\circ}22'$	$61^{\circ}22'$
$o : q = 111 : 011$	1	$28^{\circ}36'$	$28^{\circ}36'$	$28^{\circ}38'$
$m : o = 110 : 111$	2	$54^{\circ} 2' - 54^{\circ} 3'$	$54^{\circ} 3'$	$54^{\circ} 3'$
$\sigma : m' = 111 : 110$	1	$101^{\circ}11'$	$101^{\circ}14'$	$101^{\circ}18'$
$s : o = 201 : 111$	1	$27^{\circ}11'$	$27^{\circ}11'$	$27^{\circ}17'$
$s : k = 201 : 031$	2	$66^{\circ}17' - 66^{\circ}21'$	$66^{\circ}19'$	$66^{\circ}15'$
$m : k = 110 : 031$	2	$63^{\circ}31' - 63^{\circ}40'$	$63^{\circ}35'$	$63^{\circ}44'$
$m : q = 110 : 011$	6	$77^{\circ}13' - 77^{\circ}22'$	$77^{\circ}17'$	$77^{\circ}19'$

The optical character is similar to that of the preceding salt.

$$\alpha = 1.4874, \beta = 1.5580, \gamma = 1.5867.$$

$$2V = 62^{\circ}33' \text{ (calculated).}$$

Cæsium Trithionate.

For the preparation of this salt, 32 grams of cæsium persulphate were taken along with 45 grams (theory, 40.4) of strontium thiosulphate and 60 c.c. of water; the purification, etc., were carried out as before. The salt is apparently still more soluble than the rubidium compound, but by evaporation at low atmospheric temperature, well-formed crystals with highly lustrous faces were obtained. When these crystals were

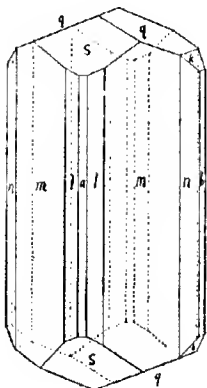
removed from the mother liquor and dried on filter-paper, they rapidly became dull and opaque, indicating that the salt had been obtained in a hydrated form. This was confirmed by the analysis of fresh crystals. For the analysis, sulphur was determined as in the preceding case, and the caesium remaining in the filtrate was determined as sulphate:

0.3090 gave 0.4554 BaSO_4 and 0.2340 Cs_2SO_4 . $\text{S} = 20.24$; $\text{Cs} = 55.65$.
 $\text{Cs}_2\text{S}_3\text{O}_6 \cdot \text{H}_2\text{O}$ requires $\text{S} = 20.20$; $\text{Cs} = 55.87$ per cent.

Using a mixture of methylene di-iodide and tetrabromoethane, the density was found to be 3.192, as the average of seven determinations (limits, 3.189 and 3.196). Molecular volume = 149.1.

A complete crystallographic examination could not be made at the

FIG. 2.



time, owing to the rapid efflorescence of the crystals, but they were proved to belong to the triclinic system.

The easy dehydration of the salt indicated that the transition temperature is low, so that it might be possible to prepare the anhydrous salt in a crystallised form for comparison with those of potassium and rubidium. This was effected without difficulty by the very slow cooling of a hot solution (about 50°) containing alcohol. The salt is not isomorphous with the other two, however, but crystallises in the triclinic system. Since the crystals which were obtained were not very well formed, the crystallographic examination did not prove very satisfactory, and the description of both forms will therefore be deferred.

When it was sought to determine the density of the anhydrous

trithionate, it was found that a whole crystal just floated on undiluted methylene di-iodide, but that after it was fractured, some of the fragments sank in the same liquid; the density would therefore appear to be very slightly higher than that of the methylene di-iodide, which we found to be 3.326.

For the analysis, the total sulphur was determined as before, and the caesium directly as sulphate on a fresh portion :

0.2953 gave 0.4566 BaSO_4 . S = 21.2.

0.1894 „ 0.1532 Cs_2SO_4 . Cs = 57.9.

$\text{Cs}_2\text{S}_3\text{O}_6$ requires S = 20.98 ; Cs = 58.07 per cent.

The Estimation of Rubidium and Caesium.

The estimation of the metals of the alkali group as sulphates by ignition with sulphuric acid is very simple in the case of the lowest member of the group, but becomes less easy with increasing atomic weight. This is due to the increasing stability of the acid sulphates and anhydrosulphates, and the increasing volatility of the normal sulphates. Various investigators have, on this account, recommended that rubidium and caesium should be determined as acid sulphate or as anhydrosulphate by heating with sulphuric acid at some definite temperature, a method which is not very convenient. We have tried another method, which promises to give satisfactory results in a simpler manner. It was based on the fact that the metals of the alkali group form with those of the alkaline-earth group definite double sulphates of the type $\text{M}_2\text{SO}_4 \cdot \text{MSO}_4$, so that there was some reason to expect that if the ignition with sulphuric acid were carried out in presence of an excess of, say, calcium sulphate, the double salt would be formed in preference to the acid sulphate or the anhydrosulphate. In that case, the excess of acid might be completely removed at a temperature sufficiently below that at which appreciable volatilisation of the double sulphate would take place without the necessity of adhering to definite limits.

To test the method, a moderate quantity of pure calcium sulphate was placed in a platinum crucible, which was then ignited and weighed. As a preliminary test, which did not require to be repeated in subsequent experiments with the same material, sulphuric acid was added and the ignition repeated; there was no change in weight. The caesium salt was next added along with sulphuric acid, and the whole gradually heated. It was found that a constant weight was attained at a low red heat, and that the increase in weight above that of the crucible and calcium sulphate alone agreed well with the quantity of caesium sulphate calculated. The method would therefore appear to be

satisfactory, but, as very few determinations have so far been made by means of it, a more extended test of its applicability still remains to be performed. The results of this we hope to communicate along with the other matters already foreshadowed.

CHEMISTRY DEPARTMENT,
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CLXIX.—*The Spontaneous Crystallisation of Solutions of some Alkali Nitrates.*

By BERNARD MOUNT JONES.

THE work recorded below was undertaken with a view to determining whether the existence of a supersolubility curve, which has been observed in several cases, is a general phenomenon, and, if possible, to throw more light on the meaning of this curve. The solutions chosen for investigation were those of potassium, rubidium, and caesium nitrates, since these salts crystallise from aqueous solution in the anhydrous condition, and their crystals form an isomorphous series. These salts are only moderately soluble in water, and the viscosity of their supersaturated solutions is probably insufficient to offer much hindrance to spontaneous crystallisation. Since they have approximately equal molecular volumes (48.1, 47.0, 52.8), the relative magnitudes of the metastable regions should be nearly independent of this quantity.

All three salts have given a well-defined supersolubility curve, marking the temperature limit above which spontaneous crystallisation of the salt phase cannot, and below which spontaneous crystallisation can, take place. The ice-supersolubility curves have been traced, also the ice-solubility curves, for solutions of rubidium and caesium nitrates, which do not appear to have been previously determined.

The method used was the same as that adopted in the investigation of sodium sulphate solutions (Hartley, Jones, and Hutchinson, this vol., 825). Weighed amounts of the nitrates (Merck) and distilled water were sealed up in small glass tubes, and then warmed until all traces of crystalline material disappeared. The tubes were then allowed to cool slowly with constant shaking in a well-stirred water (or toluene) bath, the temperature of which was falling one degree in fifteen minutes, until crystallisation took place. The process was then repeated, keeping the temperature

of the bath a long time slightly above the temperature at which crystallisation was first observed. This often had the effect of raising the observed temperature of crystallisation by one or two tenths of a degree.

The first experiments were done with tubes containing no solid matter, such as glass or garnets, to produce mechanical friction. Since it has been shown (J. Chevalier, *Min. Mag.*, 1906, **14**, 65, 142) that crystallisation in the metastable region can be brought about by crystalline fragments the crystal form of which bears no relation to that of the solid phase crystallising, it was thought advisable to avoid any possible "inoculations" of the three salt solutions by crystal fragments, such as garnets, which might have unequal effects in the three cases. The results obtained with tubes containing no solid matter at first gave indications of regular supersolubility curves. But irregularities soon began to appear, especially in the more concentrated, and therefore more viscous, solutions. The remaining experiments were done with tubes containing small irregular fragments of Jena glass, which could have no "inoculating" effect. The effect of these glass fragments was to make the phenomenon of crystallisation more definite, and generally to raise the temperature at which crystallisation took place. The thermometers used were graduated in tenths of a degree, and were standardised against a thermometer with Reichsanstalt certificate.

Crystallisation of Potassium Nitrate.

TABLE I.

Grams KNO_3	Grams H_2O	Grams KNO_3 in 100 grams H_2O	Gram-mols. KNO_3 in 100 grams H_2O	Temperature of crystallisation of KNO_3
0.5232	3.7213	14.07	0.133	-1.3°
0.9121	5.7430	15.88	0.157	0.7°
1.6474	8.2649	19.93	0.197	4.4°
0.9166	1.1798	21.93	0.217	3.1°
1.4818	5.9872	24.75	0.245	10.0°
0.9520	3.1308	30.32	0.300	16.0°
2.0709	6.8151	30.40	0.301	12.9°
1.3458	4.0779	33.03	0.328	16.4°
1.5978	4.9139	39.89	0.394	22.2°
1.1012	2.7391	40.20	0.398	20.1°
1.0573	2.6216	40.33	0.399	23.5°
1.0192	8.2195	48.61	0.481	27.0°
1.7159	3.4466	49.75	0.493	28.9°
3.7159	6.5881	56.40	0.558	29.8°
1.1128	1.8628	60.11	0.595	33.9°
3.8961	5.6896	66.90	0.662	35.5°
2.0641	2.9626	69.67	0.690	38.4°
1.7341	2.1968	78.94	0.782	42.8°
3.3483	4.1161	81.45	0.807	42.6°
3.8558	4.9242	95.81	0.949	47.6°
3.5318	3.5914	100.89	0.999	51.8°

Crystallisation of Potassium Nitrate.

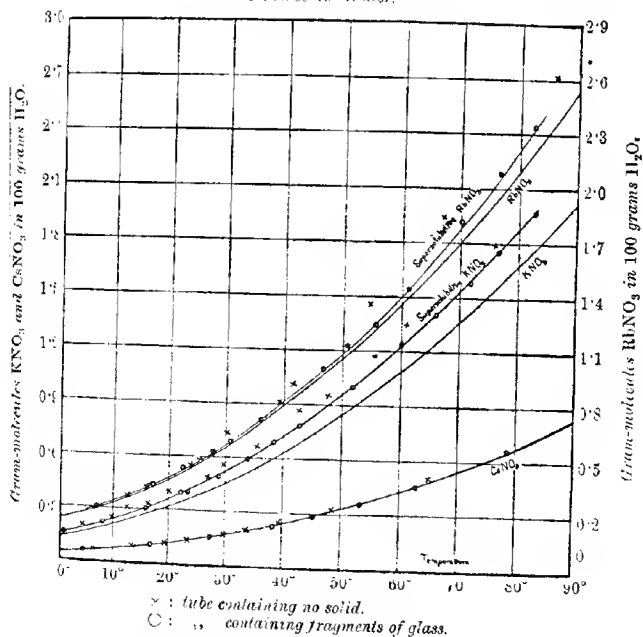
TABLE I (continued).

Grams KNO_3	Grams H_2O	Grams KNO_3 in 100 grams H_2O	Gram-mols. KNO_3 in 100 grams H_2O	Temperature of crystallisation of KNO_3
3.9358	3.3318	118.12	1.170	55.6
2.2733	1.6694	121.60	1.204	60.5 *
5.3865	3.9727	135.59	1.345	60.9
1.6092	1.1323	142.12	1.497	66.1 *
2.2153	1.3964	158.64	1.571	71.9 *
3.0732	1.7366	176.97	1.752	76.6 *
6.9816	3.8562	181.04	1.793	75.9
2.1508	1.0898	199.00	1.970	82.8 *

Table I gives the highest temperatures at which potassium nitrate crystallised from aqueous solutions of various strengths. An

FIG. 1.

Solubility and Supersolubility Curves of Potassium, Rubidium, and Cesium Nitrates in Water.



asterisk signifies that the corresponding tube contained glass fragments. The results are plotted in Fig. 1, which shows both the solubility and supersolubility curves. In the figure, \circ represents

a point obtained with a tube containing glass fragments; \times indicates a tube containing no solid matter. It will be noticed that the results obtained with glass fragments lie on a regular curve, whilst in the absence of such fragments crystallisation often did not take place until the solution was in the labile condition. The phenomenon of crystallisation was very definite in the presence of mechanical friction, successive determinations almost always agreeing within one-tenth of a degree. At the temperature of spontaneous crystallisation, a sudden shower of small crystals was produced. The supersolubility curve runs nearly parallel to the solubility curve, gradually approaching it as the concentration decreases.

Crystallisation of Rubidium Nitrate.

TABLE II.

Grams RbNO_3 .	Grams H_2O .	Grams RbNO_3 in 100 grams H_2O .	Gram-mols. RbNO_3 in 100 grams H_2O .	Temperature of crystallisation of RbNO_3 .
0.6867	2.3069	29.76	0.202	7.0*
1.4226	3.5430	40.15	0.272	12.6
0.4574	0.9630	47.50	0.322	16.2
1.6911	3.4465	49.07	0.333	16.8
0.8952	1.8032	49.64	0.337	17.3*
0.5913	0.9258	63.86	0.433	22.5*
1.1640	1.7852	65.20	0.442	24.0
2.0046	2.8240	70.98	0.482	25.6
2.7294	3.5554	76.77	0.521	27.8
1.8308	2.3464	78.03	0.529	28.0
0.9432	1.0872	86.75	0.589	30.9*
3.3627	3.5944	93.56	0.635	30.3
1.0864	1.0181	104.74	0.711	36.1*
1.2642	1.0643	118.78	0.806	39.3
2.5579	1.9118	133.79	0.908	41.5
1.3873	0.9386	145.68	0.983	46.7*
2.2046	1.3258	166.28	1.128	50.8*
1.5680	0.8528	183.86	1.247	55.1*
3.4128	1.7090	199.70	1.355	54.5
1.8726	0.8803	212.72	1.443	61.1*
2.4612	0.9170	268.39	1.821	70.0*
4.0523	1.4930	271.42	1.841	66.9
1.3324	0.4335	307.36	2.055	78.6*
1.8271	0.5297	341.93	2.340	82.4*
3.3975	0.8793	356.35	2.621	86.1

In this case, also, crystallisation in presence of mechanical friction was very definite, different readings for the same tube generally agreeing to one-tenth of a degree. Except in the case of very concentrated solutions, a shower of crystals was not, as a rule, observed. Usually about four or five small crystals would suddenly make their appearance. A shower of crystals was more often observed in tubes containing no glass fragments, in which case the "relief of supersaturation" caused by crystallisation was much

greater. The supersolubility curve is seen to run nearly parallel to the solubility curve, at a distance from it, for moderate concentrations, of about one degree. It is plotted in Fig. 1.

Crystallisation of Cæsium Nitrate.

TABLE III.

Grams CsNO_3 .	Grams H_2O .	Grams CsNO_3 in 100 grams H_2O .	Gram-mols. CsNO_3 in 100 grams H_2O .	Temperature of crystallisation of CsNO_3 .
0.4005	4.0328	9.93	0.051	-0.3°
0.3151	2.5929	12.15	0.062	4.5 *
0.3256	2.4204	13.45	0.069	6.5
0.4587	2.5396	17.85	0.092	13.6
0.3701	1.8222	20.31	0.104	16.9 *
0.9810	4.2856	22.90	0.117	19.5
0.7003	2.6008	26.92	0.138	23.5
0.9231	2.9904	30.87	0.158	27.5 *
0.5616	1.6428	34.18	0.175	29.9
0.6702	1.7038	39.33	0.202	33.8
1.0458	2.3606	44.40	0.228	38.4 *
1.9602	4.0420	48.49	0.249	39.5
1.0254	1.8426	55.65	0.235	45.3 *
1.1977	1.8959	63.17	0.324	48.5
0.9353	1.3296	70.34	0.361	53.3 *
1.5143	1.6817	90.04	0.462	62.9 *
1.1045	1.1117	99.36	0.510	65.1
1.9474	1.4969	130.10	0.667	73.7 *

It will be seen in Fig. 1 that the temperatures of spontaneous crystallisation of cæsium nitrate lie on the solubility curve within the limits of error, and the metastable region therefore disappears. The crystallisation was in all cases extremely definite, although, as is to be expected, nothing like a shower of crystals was ever observed. Instead, a few, sometimes only one or two, minute crystals appeared, too small to be properly examined with an ordinary pocket lens. They were not, as a rule, sharply defined, but presented a somewhat globular or spherulitic appearance. On lowering the temperature slightly, they grew rapidly, and other well-defined crystals would make their appearance. On raising the temperature two or three tenths of a degree, they very slowly disappeared. The effect of friction in bringing about crystallisation is seen from the figure to be much less in the case of cæsium nitrate solutions than with potassium and rubidium nitrates.

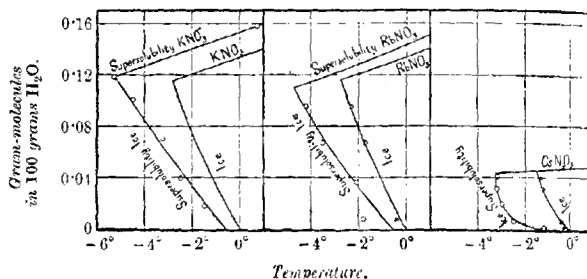
Crystallisation of Ice from Solutions of Potassium Nitrate.

TABLE IV.

Grams KNO_3	Grams H_2O	Grams KNO_3 in 100 grams H_2O	Gram-mols. KNO_3 in 100 grams H_2O	Temperature of crystallisation of ice.
0.0921	4.9387	1.86	0.018	-1.5*
0.0345	0.8717	3.95	0.039	-2.5 *
0.1222	1.7291	7.06	0.070	-3.2 *
0.1180	1.1544	10.22	0.101	-4.5 *
0.2927	2.4623	11.88	0.118	-5.3 *

These results, which show the temperatures at which ice crystallises spontaneously from dilute solutions of potassium nitrate, are plotted on a larger scale in Fig. 2. The production of the ice phase appears to be a somewhat less definite phenomenon than the production of the salt phase. The points plotted represent the highest temperatures at which, by means of vigorous shaking, the

FIG. 2.



crystallisation of ice could be induced to take place. Ice was, however, not always produced at these temperatures, there being as much as half a degree difference between some determinations with the same tube. The curve drawn cuts the temperature axis at about -0.5° , which is the temperature of spontaneous crystallisation of ice from pure water observed by Hartley, Jones, and Hutchinson (*loc. cit.*). The temperature observed by Miers and Miss Isaac (*Chem. News*, 1906, **94**, 89) was -0.4° . The highest temperature observed by the author at which ice was produced in pure water containing glass fragments was -1.2° . The value -0.5° was obtained with water containing garnets, and this fact may perhaps account for the discrepancy. Miers' value was obtained "by introducing glass, garnet, galena, or lead into the tubes." The ice- and potassium nitrate-supersolubility curves give rise, by

their intersection, to a "hypertectic" point at about -5.3° , the solution containing 0.118 gram-mols. of potassium nitrate per 100 grams of water.

Solubility and Supersolubility of Ice in Rubidium Nitrate Solutions.

TABLE V.

Grams RbNO_3 .	Grams H_2O .	Grams RbNO_3 in 100 grams H_2O .	Gram-mols. RbNO_3 in 100 grams H_2O .	Temperature of crystallization of ice.	Temperature of saturation.
0.0547	4.7057	1.16	0.008	—	-0.4° *
0.0615	4.9726	1.24	0.008	-1.8°	— *
0.1129	2.0959	5.39	0.036	-2.1	— *
0.1298	1.3046	9.94	0.067	-3.5	-1.7°
0.3574	2.5585	13.97	0.085	-4.2	-2.3° *

The ice-solubility curve was determined, using the same tubes as for the supersolubility experiments. The solutions were frozen to give a small quantity of ice, and then by suitably regulating the temperature of the bath, two temperatures were determined, one at which the ice was just dissolving, and one at which it was just growing. These temperatures differed generally by about 0.3° or 0.4° , and the mean of the two was taken to be the temperature of saturation. The results, represented thus: Δ , are plotted in Fig. 2. As in the case of dilute potassium nitrate solutions, the spontaneous production of ice was of a somewhat uncertain character, especially in the more dilute solutions. For instance, one tube containing 0.008 gram-mols. of rubidium nitrate per 100 grams of water, crystallised on one occasion at -1.8° , and on another not before -2.8° . The supersolubility curve for ice is drawn through the highest observed temperatures, and, as before, is seen to cut the temperature axis at about -0.5° . The eutectic and "hypertectic" points are respectively about -2.7° and -4.7° , the solutions containing 0.116 and 0.110 gram-mols. per 100 grams of water.

Solubility and Supersolubility of Ice in Caesium Nitrate Solutions.

TABLE VI.

Grams CsNO_3 .	Grams H_2O .	Grams CsNO_3 in 100 grams H_2O .	Gram-mols. CsNO_3 in 100 grams H_2O .	Temperature of crystallization of ice.	Temperature of saturation.
0.0682	3.8347	0.21	0.001	1.2	-0.3° *
0.0599	4.6619	1.28	0.007	-2.5	-0.4° *
0.0968	2.4254	3.99	0.020	-3.0	— *
0.1181	1.9692	6.01	0.031	-3.2	-1.2°
0.2248	2.8096	8.00	0.041	-3.2	-1.3° *

The solubility curve was determined as above, and is plotted in Fig. 2. The spontaneous production of ice again seemed to be rather sluggish, and the ice-supersolubility curve takes an unusual form, although cutting the temperature axis at about -0.5° . The eutectic and "hypertectic" points are at -1.5° and -3.3° , with concentrations of 0.046 and 0.044 gram-mols. per 100 grams of water respectively.

Discussion of Results.

The above results are based on about 280 experiments, in all of which spontaneous crystallisation took place. The results obtained with tubes containing glass lie on fairly regular curves, and in no case did crystallisation take place appreciably within the metastable region as defined by these curves. The experiments afford additional evidence that as far as capacity to crystallise is concerned, supersaturated solutions show an abrupt change in passing from the metastable to the labile state.

Although the molecular solubility of potassium nitrate is intermediate between that of rubidium and caesium nitrates, the size of the metastable region follows the molecular weight of the salts, the metastable range for rubidium nitrate being intermediate in size between those for potassium and caesium nitrates. The supersolubility of these three isomorphous salts appears to afford another instance of periodicity of properties. Taking equal molecular concentrations of the three salts, say, 0.6 gram-mols. of salt per 100 grams of water, the metastable ranges are respectively about 4° , 1° , and 0° . In view of the fact that caesium nitrate is the most strongly ionised of all salts, and is the least liable of all salts to hydration in solution (Abegg and Bodländer, *Zeitsch. anorg. Chem.*, 1899, **20**, 453; W. Biltz, *Zeitsch. physikal. Chem.*, 1902, **40**, 217), it is interesting that it should be the only salt so far known to possess no measurable metastable region. Theoretically, there must be supersaturation before crystallisation can take place, but in the case of caesium nitrate the necessary amount of supersaturation is too small to be measured by the method used. Whether this fact is in any way connected with the lack of hydration of the caesium nitrate molecules, there are insufficient data as yet to decide. On general grounds, hydration of the molecules of salts which crystallise in the anhydrous state would be expected to hinder crystallisation. This is in accordance with the observed order of magnitude of the metastable regions of the three salts investigated. With a view to seeing how the metastable range depends on the energy changes accompanying crystallisation, the

author hopes to determine shortly the heats of crystallization of these salts.

Summary.

1. Supersaturated solutions of the nitrates of potassium, rubidium, and caesium, freed from crystal nuclei, crystallise at definite temperatures when subjected to mechanical friction.
2. The supersolubility curves for the three salts and the corresponding ice-supersolubility curves have been traced.
3. The ice-solubility curves for dilute solutions of rubidium and caesium nitrates have been traced.
4. The metastable range is greatest for potassium nitrate and least for caesium nitrate, the size of the metastable region decreasing as the molecular weight increases.

The author wishes to thank Mr. Harold Hartley, Balliol College, Oxford, for valuable suggestions.

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CLXX.—*The Relation between Absorption Spectra and Chemical Constitution. Part IX. The Nitroso- and Nitro-groups.*

By EDWARD CHARLES CYRIL BALY and CECIL HENRY DESCH.

THE present communication deals with the absorption spectra of compounds containing the groups $-\text{NO}$ and $-\text{NO}_2$, both of which are known to exert a great influence on the colour of organic compounds into which they are introduced. With the object of eliminating as far as possible the effect of conjugation with other groups, the simplest aliphatic and inorganic compounds available were chosen for investigation. Since the position of the absorption band is found to be influenced greatly by the nature of the atom to which one of the above groups is directly linked, compounds containing those groups linked to carbon, nitrogen, oxygen, and sulphur have been examined.

The method of observation adopted is in principle the same as that employed in previous papers of this series, but it has been found necessary to introduce several important modifications. The absorption bands of many of the compounds studied fall high up in the visible region of the spectrum, and with small dispersion their

accurate measurement is difficult or impossible. A new quartz spectrograph by Hilger, giving a very extended spectrum, has therefore been installed in the spectroscopic laboratory of University College. In this instrument only a single quartz prism is used, and the large quartz lenses are so cut as to bring the whole spectrum to a focus on a surface which is very nearly plane, but highly inclined, to the optical axis. This high inclination gives a large dispersion, the photograph of the spectrum of the iron arc obtained in this way being 18 cm. long. The plates used are 25 by 10 cm. in size, the shape of the dark slide being such as to bend them to the extent of 2 mm. in the middle, this giving a sharp focus over the whole length. Wratten and Wainwright's "Allochrome" plates have been used, except when it was desired to photograph in the extreme red region, in which case the special "spectrum" plates of the same makers, sensitive up to $1/\lambda 1300$, have been employed. As the source of light, we have found the iron and nickel spark preferable in many cases to the iron arc, the distribution of intensity being much more uniform. When focussed on to the slit by means of a quartz condensing lens, carried on an optical bench attached to the base of the spectrograph, an exposure of ten seconds is sufficient, using either the arc or the spark, even when the thickness of coloured liquid is considerable. The dark slide is moved by means of rackwork, and 20 spectra are taken on each plate.

It was found necessary to adopt a different arrangement when photographing the spectra of coloured nitroso-compounds. The colour being green or blue, the absorption band falls in the extreme red, at a point at which the iron spectrum fails. Since a suitable line spectrum extending into this region could not be found, it was necessary to use a source of light giving a continuous spectrum, with some device for fixing the wave-lengths at different points on the plate. This may be done by means of interference fringes. A Nernst filament, or the crater of a carbon arc, the latter being found the more convenient, is focussed on the slit by means of the condensing lens in the usual way. A Fabry-Pérot interference plate is then interposed in the path of the rays. This consists of two thinly-silvered pieces of plate glass, cemented together so that their silvered surfaces are separated by a thin layer of air. When the plate is placed normally to the incident beam, the continuous spectrum is seen to be crossed by a number of parallel dark fringes, and by adjusting the plate, these may be made accurately vertical. They then take the place of the lines in a line spectrum, although the method of calibration is different. The fringes are counted instead of being measured, their numerical position being propor-

tional to their oscillation-frequency, so that the distance, for example, from a fringe arbitrarily selected to the tenth in order from it, represents the same difference of oscillation-frequency as that from the tenth to the twentieth. Two fixed points are then sufficient for calibration. When a carbon arc is employed, one of those is already given by the head of the first band at $1/\lambda 2574$, which is always well marked in the photographs. For the other, a single line, such as the line at $1/\lambda 1701$ given by a helium vacuum tube, is the most suitable. It is best to make two exposures of the fringes without any intervening liquid, one at the top and one at the bottom of each plate, and to superimpose the helium line on each of these. The wedge covering the slit is opened a little for this purpose, so that the line slightly overlaps the spectrum. In reading the negative, lines are ruled with a fine point through these standard points, crossing the intermediate spectra, and the fringes are counted from these fixed datum lines. It facilitates counting if lines are also ruled at every fifth or tenth fringe. The oscillation-frequencies of intermediate fringes are obtained by graphical interpolation, the relation between number of fringe and oscillation-frequency being strictly linear. It is necessary to repeat the calibration with each plate, as the position of the fringes varies with the temperature, owing to the change in thickness of the film of air. With the interference plate employed in these experiments, the distance between two adjacent fringes represents a difference of oscillation-frequency of about 16.

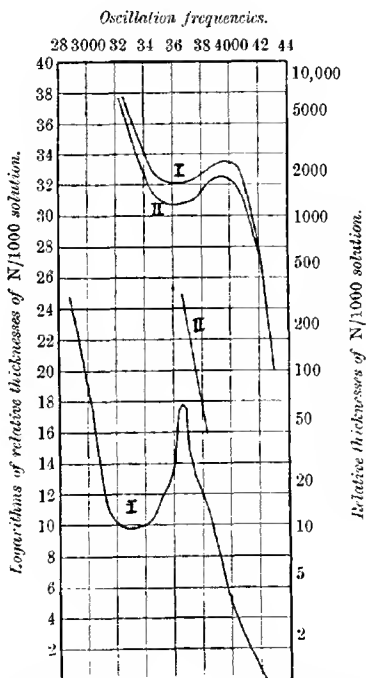
Nitro-paraffins.

Nitromethane and nitroethane give a shallow absorption band at $1/\lambda 3600$ when examined in $N/10$ solution in alcohol (Fig. 1). The addition of sodium ethoxide precipitates the sodium salt, so the effect of alkali has been studied in 50 per cent. alcohol. The addition of one equivalent of alkali removes the band, but on keeping the solutions overnight and again examining, the nitromethane is found to have developed a new band at $1/\lambda 3300$ at a much higher dilution. The alkaline solution of nitroethane, on the other hand, remains unchanged for many days. After photographs of these spectra had been taken, a paper on the absorption spectra of nitro-compounds by E. P. Hedley appeared (*Ber.*, 1908. 41, 1195), in which the mononitro-paraffins were stated to exhibit only continuous absorption, the absorption being increased by the addition of alkali, but without the production of a band. In view of this discrepancy, the experiments were repeated with freshly-distilled nitromethane and nitroethane, boiling within one-tenth of

a degree, but the spectra observed only confirmed our previous results. We therefore conclude that the mononitro-paraffins show a small, but distinct, absorption band.

The increased absorption due to the introduction of the nitro-group into a hydrocarbon has been further studied by a comparison of styrene, $C_6H_5 \cdot CH:CH_2$, with ω -nitrostyrene, $C_6H_5 \cdot CH:CH \cdot NO_2$.

FIG. 1.



I: Nitromethane.

II: Nitroethane.

Upper curves: In alcohol.

Lower .. : In dilute alcohol with alkali, after remaining overnight.

(Fig. 2). Whilst styrene gives an absorption curve with only a small extension at $1. \lambda 3600$, its ω -nitro-derivative has a large absorption band at $1. \lambda 3400$.

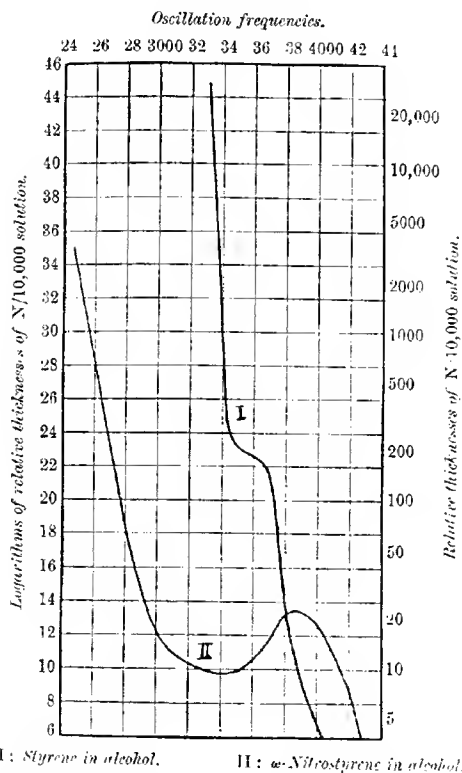
Nitroamides.

Passing now to compounds in which the nitro-group is directly linked to a nitrogen atom, the simplest representative is nitroamide.

$\text{NH}_2\cdot\text{NO}_2$. This does not show any selective absorption (Fig. 3), the compound possibly behaving in solution as an internal salt, but the introduction of a methyl group yielding methylnitroamide, $\text{NHMe}\cdot\text{NO}_2$, gives rise to a well-marked absorption band.

Carbamide is remarkably diactinic, a normal solution transmitting practically the whole spectrum, and urethane shows only a

FIG. 2.



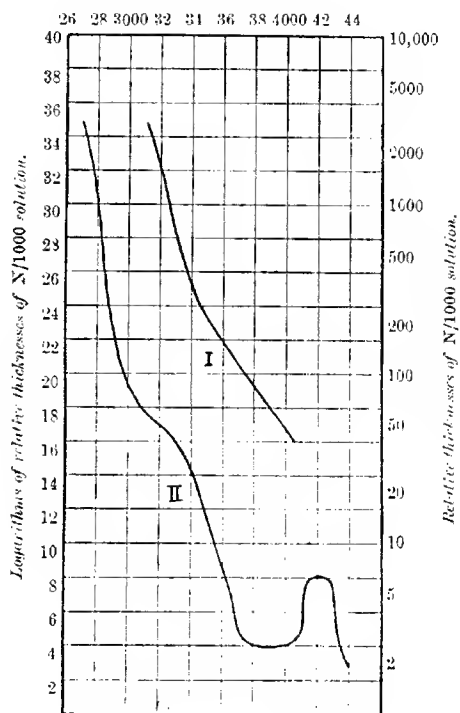
small continuous absorption. On the other hand, nitrocarbamide, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NO}_2$ (Fig. 4), shows an increased absorption, and on addition of alkali in excess a rapid extension of the spectrum, or incipient band, appears in $N/1000$ solution. With nitrourethane, $\text{OEt}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$, the addition of alkali produces a well-marked band at $1/\lambda 3900$. All these compounds were prepared by the

methods described by Thiele and Lachmann (*Annalen*, 1895, 288, 267).

Nitroguanidine, $\text{NH}_2\text{C}(\text{NH}_2)\cdot\text{NH}\cdot\text{NO}_2$, is so sparingly soluble in alcohol or water that the spectrum of the free substance could not be examined. Solutions in aqueous or alcoholic alkali showed only continuous absorption.

FIG. 3.

Oscillation frequencies.



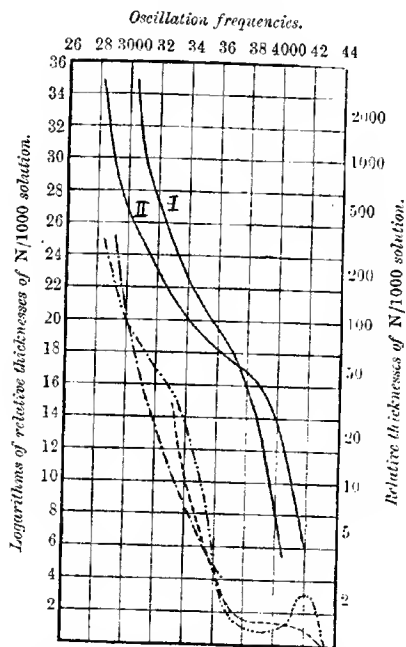
I: Nitroumid in alcohol. II: Methylnitroumid in alcohol.

Nitroso-compounds.

The only true nitroso-compounds known in the aliphatic series are those in which the nitroso-group is attached to a tertiary carbon atom, and such compounds are intensely blue in colour. *tert.*-Nitroso-isopropylacetone was selected as the most stable representative of its class. When prepared by the oxidation of diacetoneamine oxalate

with Caro's reagent (Bamberger, *Ber.*, 1903, **36**, 685), it forms colourless crystals, which may be weighed without loss, and dissolve to form colourless solutions of the bimolecular form. The colour of such solutions gradually becomes blue, owing to depolymerisation, but the aqueous solution remains colourless for a considerable time unless heated, and in

FIG. 4.



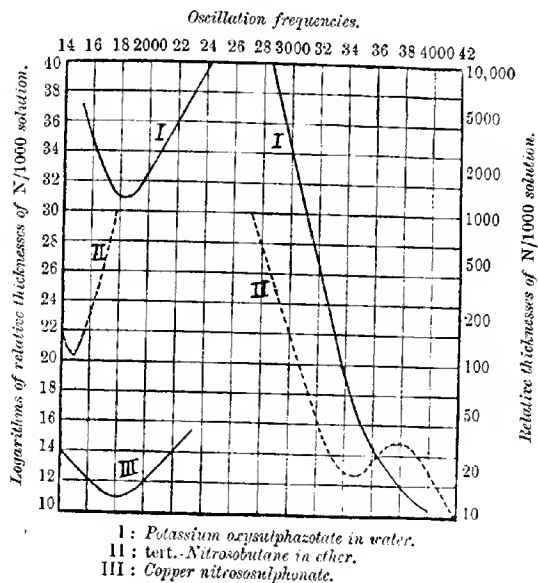
Full curve I: Nitrocarbamide in alcohol.
 Dotted curve: Nitrocarbamide with alkali.
 Dot and dash curve: Nitroguanidine in alkali.
 Full curve II: Nitrourethane in alcohol.
 Dash and two dots curve: Nitrourethane with alkali.

this state shows a single absorption band in the ultra-violet (Fig. 5). After heating the solution several times and cooling, this band is found to have diminished greatly in persistence, and a new band appears in the red. It is this band which gives rise to the blue colour, and characterises the unimolecular form of the compound. Even very thick layers of an $N/10$ solution continue to transmit the blue rays, so that it was not found possible to

the same position as in the spectrum of the aliphatic nitroso-compounds.

Two inorganic compounds of strikingly blue colour, containing the group $>\text{N}:\text{O}$, were also examined. The first of these, the so-called potassium oxysulphazotate, is readily prepared by the oxidation of potassium hydroxylaminedisulphonate with potassium permanganate (Raschig, *Ber.*, 1907, **40**, 4580). The fact that it forms yellow crystals in the solid state, but dissolves in water to a purple solution deceptively like the permanganates in colour,

FIG. 6.

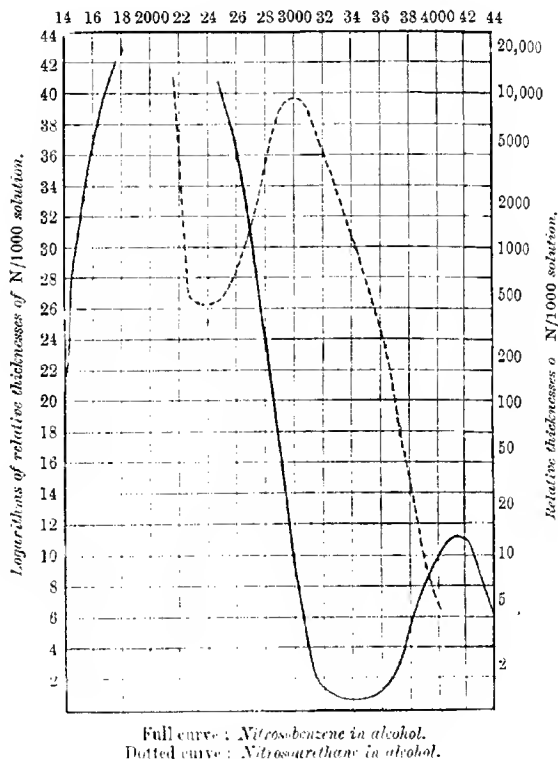


suggests an analogy to the nitroso-compounds. Hantzsch and Semple (*Ber.*, 1895, **28**, 2744) have therefore represented it as $\text{O}:\text{N}(\text{SO}_3\text{K})_2$, the yellow form being bimolecular. It will be noticed that the unimolecular formula involves quadrivalent nitrogen. The spectrum (Fig. 6, curve I) shows a single large absorption band, having its head at $1/\lambda 1850$. There is no band in the ultra-violet.

Another blue nitrogen compound is the substance obtained on reducing nitrosulphonic acid with mercury or copper, giving rise to the transient blue coloration observed in the nitrometer. Unfor-

tunately, the free acid and its mercury salt are too unstable to allow of the examination of their spectrum, but the copper salt is comparatively stable in concentrated sulphuric acid solution (Raschig, *loc. cit.*). The spectrum shows a broad band in the red (Fig. 6, curve III). The concentration of the solution was not

FIG. 7.
Oscillation frequencies.

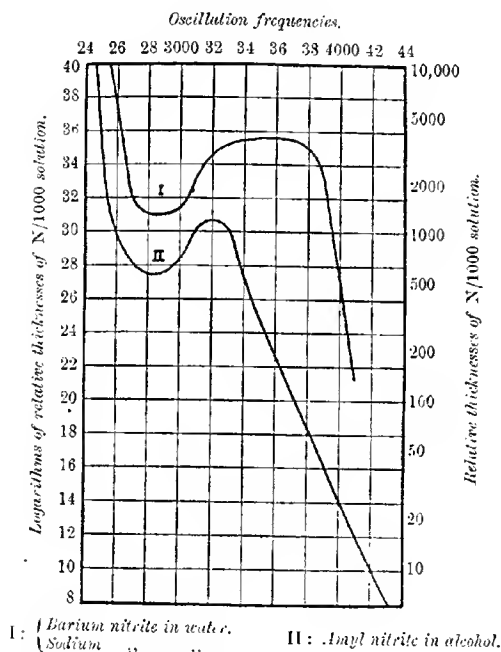


determined, and as much unreduced nitrosulphonic acid was present, it was not thought necessary to examine the ultra-violet region. As a part of the blue colour may be due to the copper, the spectrum of copper glycine, chosen as a typical blue complex salt of copper, has also been examined. The band falls within that of copper nitrosulphonate, and probably does not disturb the position

of the band due to the latter. A solution of nitrosulphonic acid, $\text{NO}_2\text{SO}_3\text{H}$, in sulphuric acid shows continuous absorption (curve V in Fig. 9). The nitrososulphonic acid obtained by its reduction has been represented as having the constitution $\text{O:N} \begin{smallmatrix} \text{OH} \\ \text{SO}_3\text{H} \end{smallmatrix}$, which is in agreement with the similarity of its spectrum to that of the oxysulphazotates.

The spectra of the metallic nitrates have been examined by

FIG. 8.

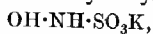


Hartley.* The nitrites give a well-marked absorption band in $N/10$ solutions (Fig. 8), the band lying much nearer to the red than the corresponding nitrate band. Sodium, potassium, and barium nitrites give identical spectra. An alcoholic solution of amyl nitrite shows a band in the same position, differing in this respect from the esters of nitric acid, which do not exhibit selective

* Trans., 1902, **81**, 556; 1903, **83**, 221, 658. For earlier observations, see Stokes, *Phil. Trans.*, 1862, **152**, 599; Soret, *Compt. rend.*, 1878, **86**, 798.

as an incipient band. The salt was prepared by digesting Kahlbaum's preparation of the barium salt with an equivalent solution of sodium sulphate.

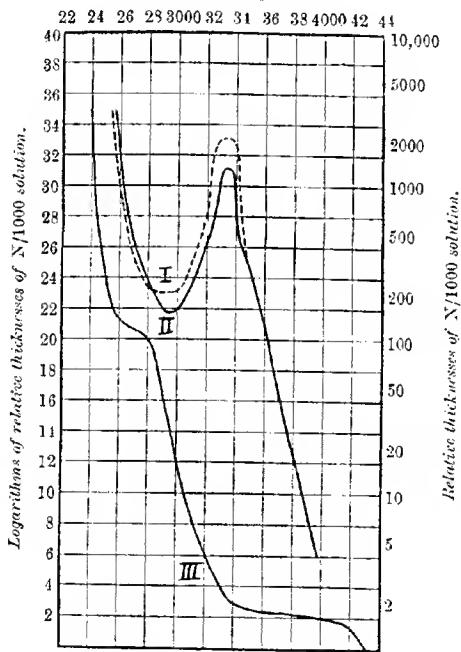
Hydroxylamine and potassium hydroxylaminesulphonate,



are remarkably diactinic, even in concentrated solutions. Potass-

FIG. 10.

Oscillation frequencies.



- I: Diethylnitrosoamine in alcohol.
 II: Dimethylnitrosoamine "
 III: Phenylmethylnitrosoamine in alcohol.

ium hydroxylaminedisulphonate (oximidosulphate), $\text{OH}\cdot\text{N}(\text{SO}_3\text{K})_2$, shows a small general absorption, which is increased on the addition of alkali, but without the production of a band (Fig. 9, curves II and IIa). Potassium nitrosulphate, $\text{N}(\text{SO}_3\text{K})_3$, is so sparingly soluble that only a very dilute solution could be examined; it shows small general absorption.

Nitrosoamines.—Alcoholic solutions of methyl- and ethyl-nitrosoamine show a strong band (Fig. 10). Phenylmethylnitrosoamine shows a small extension near $1/\lambda 2700$, and a rapid extension from $1/\lambda 3400$ — 4200 in $N/1000$ solution. Dobbie and Tinkler (*Trans.*, 1905, **87**, 273) found a shallow absorption band in this position, but although the substance was purified by distillation, followed by repeated freezing, we were unable to observe more than a horizontal extension.

The absorption spectrum of nitrosourethane, $\text{OEt}\cdot\text{CO}\cdot\text{NH}\cdot\text{NO}$, prepared by Thiele and Lachmann's method (*loc. cit.*), is shown in Fig. 7, curve II. The marked yellow colour of this compound is due to a strong absorption band at $1/\lambda 2400$.

We reserve for the present any discussion of the theoretical bearing of the results, but it has now been established that the nitro- and nitroso-groups give rise to definite selective absorption, the oscillation-frequency of which is remarkably low in the case of nitroso-compounds, and that the position of the band is greatly influenced by the nature of the atom to which the group is directly linked.

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CXXI.—*The Synthesis of Complex Acridines.*

By PERCY CORLETT AUSTIN.

THE researches during the past decade on the constitution of the morphine group of alkaloids lend peculiar interest to the study of the more complex heterocyclic compounds, especially of those derived from phenanthrene. The subject has already attracted the attention of chemists; thus Hinsberg and Garfunkel (*Annalen*, 1896, **292**, 264), J. Schmidt and Kämpf (*Ber.*, 1902, **35**, 3120), Calhane and Wheeler (*Amer. Chem. J.*, 1899, **22**, 457), and others have investigated *p*-diazines derived from phenanthrene; a phenanthroxazine has also been described by Bamberger and Grob (*Ber.*, 1901, **34**, 533), and quite recently Herschmann (*Ber.*, 1908, **41**, 1998) has succeeded in obtaining 9:10-phenanthraquinoline from 9-aminophenanthrene by Skraup's method. The experiments described in the present paper deal with acridines derived from

phenanthrene and from fluorene, which contains a triple ring system analogous to that of the former substance.

Complex acridines have been previously investigated by the present author, in conjunction with Prof. Senier (compare Senier and Austin, *Trans.*, 1906, **89**, 1387; 1907, **91**, 1233, 1240; 1908, **93**, 63), but the most complex derivatives examined were those of the phenonaphthacridines and of the dinaphthacridines. The methods devised for the preparation of these substances have now been utilised for the production of the acridines derived from phenanthrene and fluorene; these are:

(1). The condensation of an amine with methylene dihalides (Senier and Goodwin, *Trans.*, 1902, **81**, 280).

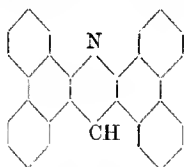
(2). The condensation of a mixture of an amine and α -naphthol with methylene dihalides (Senier and Austin, *Trans.*, 1907, **91**, 1240; Senier and Compton, *Trans.*, 1907, **91**, 1927).

In the case of phenophenanthracridine, another method has been applied, namely:

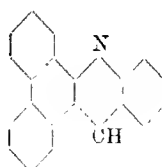
(3). The condensation of phenanthraquinone and *o*-nitrobenzyl chloride in presence of stannous chloride; this is an adaptation of Baezner's method (*Ber.*, 1904, **37**, 3077).

In applying the first of these methods to the production of diphenanthracridines, 9-aminophenanthrene was chosen as the most readily obtainable of the isomeric aminophenanthrenes. On condensing this substance in the usual manner with methylene diiodide, a diphenanthracridine is formed, which, from the nature of the reaction, must have the structure (I).

The product of the third method of synthesis must be a phenophenanthracridine of the structure (II).

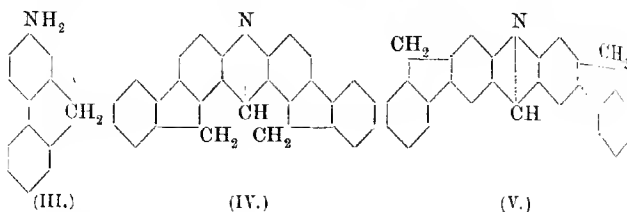


(I.)

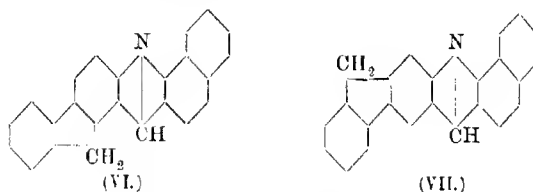


(II.)

Turning to the acridines derived from fluorene, it is evident that on account of the structure of the amine employed, 2-amino-fluorene, there is room for doubt as to the constitution of the products, for when 2-amino-fluorene (III) is condensed with methylene dihalides the product may have either of the structures (IV) and (V).



Again starting with 2-aminofluorene (III), and submitting this to condensation with methylene di-iodide and α -naphthol, the fluorenenaphthacridine which is formed might be represented by either of the following formulæ, (VI) and (VII):



At present no definite evidence in favour of one or other of these formulæ can be adduced, but experiments are in progress to effect the fission of the methylene ring system in the fluorene nucleus of these substances, and it is hoped that by suitable treatment of the products, derivatives of acridine itself, with substituents in known positions, will be obtained.

1. Preparation of 9-Aminophenanthrene.

This compound has been prepared by J. Schmidt and Strobel (*Ber.*, 1901, **34**, 1461) from 9-nitrophenanthrene by reduction, and also by J. Schmidt and Ladner (*Ber.*, 1904, **37**, 3575) by the reduction of 10-bromo-9-nitrophenanthrene. The latter method is to be preferred, but the yield is still far from satisfactory. In this method of preparation several steps are involved; first, the direct addition of bromine to phenanthrene; secondly, the conversion of phenanthrene dibromide into monobromophenanthrene; thirdly, the nitration of the latter and the separation of pure 10-bromo-9-nitrophenanthrene from by-products; and lastly, the reduction of 10-bromo-9-nitrophenanthrene to 9-aminophenanthrene. Since useful modifications of the methods described in the literature have been introduced, during the present experiments, into each stage of the reaction, the process adopted is here described.

Bromination of Phenanthrene.—Various samples of commercial phenanthrene were first used, but the results were seldom satisfactory, owing to the presence of anthracene, which formed dibromoanthracene. The solvents formerly used were carbon disulphide and ether. Ether gives uncertain results, and the use of carbon disulphide in large quantity is both unpleasant and dangerous. Very good results were obtained by dissolving pure dry phenanthrene (1 mol.) in commercial carbon tetrachloride (dried with potassium carbonate), and adding to the cooled solution dry bromine (2 atoms), dissolved in the same solvent. The bromine was previously dried over sulphuric acid and distilled. In this way the fuming of the liquid, owing to the liberation of hydrogen bromide, was greatly reduced. The somewhat unstable phenanthrene dibromide soon crystallised as a yellow solid.

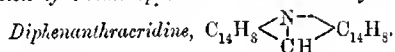
Preparation of 10-Bromophenanthrene.—The dibromide was immediately transferred to a beaker and melted by heating on the water-bath until the copious fumes of the hydrogen bromide ceased. 10-Bromophenanthrene remained as an oil, which solidified on cooling to a mass of crystals. The latter may be recrystallised from light petroleum. Thirty-two grams of phenanthrene gave 20 grams of bromophenanthrene.

Nitration of 10-Bromophenanthrene.—The nitration, as described by J. Schmidt, gives a mixture of 10-bromo-9-nitrophenanthrene and 3-nitrophenanthraquinone, which is not easily separated into its constituents. It is better to use a slight excess of the strongest fuming nitric acid. Instead of heating the mixture for twenty minutes, 10-bromophenanthrene was dissolved in hot glacial acetic acid containing a little acetic anhydride, a slight excess of nitric acid was added, and the mixture was cooled at once without further heating. A yellow solid separated, which, when freed from the mother liquor, was treated with boiling toluene and filtered from the undissolved residue. The latter proved to be 3-nitrophenanthraquinone. From the filtrate a yellow solid crystallised, which melted at about 195°. Further fractionation gave no purer product. Eventually a very pure specimen of 10-bromo-9-nitrophenanthrene was obtained by the following method, which was indicated in the investigation of the action of various reducing reagents on it. The impure 10-bromo-9-nitrophenanthrene was suspended in methylated spirit containing a little stannous chloride in solution. The liquid immediately became red. It was boiled for about two hours under a reflux condenser. The main portion of the solid remained undissolved, but the solution became paler. On cooling, the liquid was filtered off, and the residue recrystallised from benzene. Pale yellow crystals of 10-bromo-9-nitro-

phenanthrene were obtained, melting at 209° . The yield was, however, small.

Reduction of 10-Bromo-9-nitrophenanthrene.—J. Schmidt's method of reduction by using stannous chloride and glacial acetic acid gave very poor results. Other reducing agents, such as sodium and iron, were used, without obtaining the desired result. With zinc dust and ammonia, however, the substance was found to be reduced easily. Five grams of 10-bromo-9-nitrophenanthrene were suspended in about 200 c.c. of methylated spirit, and 12 grams of zinc dust were added. The mixture was heated for about four hours on the water-bath under a reflux condenser. At short intervals a few c.c. of concentrated ammonia were added, until about 40 c.c. altogether had been used. The hot red liquid was filtered from the solid, evaporated to a small bulk, and diluted with water. A white solid separated, which was collected, dried, and recrystallised from light petroleum, in which it is only sparingly soluble. Long, straw-coloured needles, turning darker in the air and melting sharply at 138° , were obtained. They were identical with 9-aminophenanthrene described by J. Schmidt.

2. Condensation of 9-Aminophenanthrene and Methylene Dichlorides:



Methylene dichloride was first used. This was found to react at a high temperature in sealed tubes. A dark brown powder, having a very high melting point, was obtained, and the yield was extremely poor. With methylene di-iodide, however, a satisfactory result was obtained. Equimolecular proportions of methylene di-iodide and 9-aminophenanthrene were heated together in a test-tube in an oil-bath. When the temperature of the bath reached 150° , the contents of the test-tube suddenly solidified, and the heating was discontinued. On treating the substance with alcoholic potash to remove halogen, and with acetone to remove any oily impurity, a pale yellow solid was obtained, which could be recrystallised from nitrobenzene. It is practically insoluble in the usual organic solvents, and does not melt below 320° . It was necessary to distil the solid under diminished pressure in order to obtain it sufficiently pure for analysis. It distils easily and without much decomposition:

0.1235 gave 0.4138 CO_2 and 0.0540 H_2O . $C=91.38$; $H=4.85$.

$C_{20}H_{17}N$ requires $C=91.82$; $H=4.48$ per cent.

3. *Condensation of Phenanthraquinone and o-Nitrobenzyl Chloride in presence of Stannous Chloride: Phenophenanthracridine,*



Four grams of phenanthraquinone were suspended in about 30 c.c. of boiling methylated spirit containing 30 grams of stannous chloride in solution. Twenty c.c. of concentrated hydrochloric acid were gradually added, and the liquid was boiled until no undissolved residue was left. During the latter process the solution became almost black. Three grams of *o*-nitrobenzyl chloride were added carefully in very small portions, and the heating was continued on the water-bath for five or ten minutes. Even at this temperature a dark brown solid separated. When cold, the mixture was filtered, and the solid residue was washed with methylated spirit and then once with a little cold acetone. The solid was then treated with boiling concentrated aqueous potassium hydroxide, which produced a yellow colour. Cold water was added, and the alkaline liquid was filtered off. The residue was well washed with cold water, and with a little acetone, to remove any black impurity still remaining. About 5 grams of a yellow powder were obtained in this way. The substance was recrystallised from benzene, from which it separated in bright yellow needles, melting at 204°. Analyses showed that it was not quite pure, but, on distilling it under diminished pressure and recrystallising again from benzene, satisfactory results were obtained. The melting point remained unaltered. Solutions in benzene, toluene, or glacial acetic acid are fluorescent:

0.1317 gave 0.4350 CO₂ and 0.0581 H₂O. C=90.08; H=4.90.

C₂₁H₁₃N requires C=90.32; H=4.66 per cent.

The compound is therefore a *phenophenanthracridine*.

4. *Preparation of 2-Aminofluorene.*

Diels prepared 2-aminofluorene (*Ber.*, 1901, **34**, 1759) by nitrating fluorene and reducing the nitro-compound with zinc dust and calcium chloride, but it is more convenient to reduce the nitrofluorene with stannous chloride. Ten grams of finely-ground 2-nitrofluorene were suspended in 100 c.c. of methylated spirit. Thirty-five grams of stannous chloride were added, and the mixture was boiled under a reflux condenser until a clear solution was obtained, after which about 25 c.c. of concentrated hydrochloric acid were gradually added, and the boiling continued for about three hours. The addition of hydrochloric acid caused a white

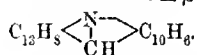
precipitate to form, which, however, slowly dissolved. On cooling the liquid, a white double salt separated. This was collected, treated with excess of boiling aqueous sodium hydroxide, and then again collected. The residue was extracted two or three times with boiling methylated spirit, and filtered from an insoluble residue. On cooling the filtrates, white needles of 2-aminofluorene, melting at 129°, separated. They could be further purified by recrystallisation from benzene.

5. *Condensation of 2-Aminofluorene with Methylene Di-halides.*

2-Aminofluorene reacted with methylene dichloride in a sealed tube heated to 250°. A non-crystallisable, brown powder was obtained, which did not melt below 300°, and which could not be purified by recrystallisation nor by distillation. Methylene diiodide, however, reacts very energetically with 2-aminofluorene when heated. The two substances were warmed together in a test-tube immersed in an oil-bath, when it was found that the reaction began at about 120°. The contents of the tube were treated in the same manner as in the case of the corresponding experiment with 9-aminophenanthrene, but the product could not be purified. On distillation under reduced pressure, it decomposed, and no suitable solvent could be found from which to recrystallise it. It was therefore not analysed. It was insoluble in water, alcohol or light petroleum; sparingly soluble in boiling acetone or in boiling ethyl acetate, with slight fluorescence, and readily so in benzene, toluene or cold pyridine.

6. *Condensation of a Mixture of 2-Aminofluorene and α -Naphthol with*

Methylene Di-iodide: Fluorene- $\overset{\text{N-}\alpha}{\underset{\text{CH-}\beta}{|}}$ -naphthlacridine,



This reaction is much more easily controlled than that between methylene diiodide and 2-aminofluorene alone. Equimolecular proportions of α -naphthol and 2-aminofluorene were heated together in an open test-tube in an oil-bath. One molecular proportion of methylene diiodide was then added, when it was found that the contents of the tube solidified at about 143°. As soon as this occurred, heating was discontinued, and the contents of the tube were treated with boiling methylated spirit until almost the whole of the substance was dissolved. Excess of aqueous potassium hydroxide was added to the solution, when a solid separated. The latter was collected, washed with water and acetone, dried,

distilled under reduced pressure, and recrystallised two or three times from toluene. Yellow needles, melting at 259°, were obtained,

which, on analysis, proved to be fluorene-^{N-α}₁-CH-β-naphthacridine.

Great care had to be taken during the analysis to avoid an incomplete combustion of the carbon:

0.1076 gave 0.3584 CO₂ and 0.0495 H₂O. C=90.84; H=5.11.

C₂₁H₁₅N requires C=90.85; H=4.73 per cent.

In conclusion, I desire to express my thanks to Prof. Collie and to Assistant-Prof. Smiles for much valuable advice during the course of this investigation.

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Organic Chemistry.

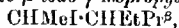
Exact Analysis of Marsh Gas. Dissociation of Several Hydrocarbons Effected in the Eudiometer for Measuring Fire-damp. NESTOR GRÉHANT (*Compt. rend.*, 1908, 146, 1199—1200).—A sample of gas collected at the bottom of a shaded pool of water contained 67.7% of methane.

Samples (60 c.c.) of methane, ethylene, and acetylene were introduced respectively into three of the author's eudiometers for measuring fire-damp ("eudiomètre-grisonmètre"), in which spirals of platinum wire are suspended. When these spirals are made red-hot by passing an electric current through them 500—600 times, the methane dissociates gradually, expanding to twice its original volume, hydrogen being liberated and a small amount of carbon deposited; the ethylene gives some small drops of tar, deposits carbon on the walls of the vessel; and increases slightly in volume, whilst the acetylene inflames at the first passage of the current, giving an abundant deposit of carbon on the spiral and on the eudiometer walls, and decreasing considerably in volume. E. H.

Diethylisopropylmethane [β -Methyl- γ -ethylpentane]. LATHAM CLARKE (*Amer. Chem. J.*, 1908, 39, 572—579).—In an earlier paper (Abstr., 1907, i, 169) an account has been given of the preparation of a new octane (δ -methylheptane). Another octane, β -methyl- γ -ethylpentane (diethylisopropylmethane), has now been synthesised by two different methods.

γ -Ethyl β -pentanone (diethylacetone), on treatment with magnesium methyl iodide, yields β -methyl- γ -ethyl- β -pentanol, $\text{OH}\cdot\text{CMe}_2\cdot\text{CHEt}_2$, b. p. $156^\circ/760$ mm., which has a strong aromatic odour. On treating this compound with iodine and red phosphorus, β -iodo- β -methyl- γ -ethylpentane, $\text{CMe}_2\text{I}\cdot\text{CHEt}_2$, is obtained, which on reduction with zinc and hydrochloric acid is converted into β -methyl- γ -ethylpentane.

Ethyl ethylisopropylacetate, $\text{CH}_3\cdot\text{CO}\cdot\text{CEtPr}^\beta\cdot\text{CO}_2\text{Et}$, b. p. $224^\circ/760$ mm., prepared by Conrad and Limpach's method (Abstr., 1878, 781), is a colourless liquid with a pleasant pine-wood-like odour. On hydrolysis with potassium hydroxide, it yields γ -isopropyl- β -pentanone (ethylisopropylacetone), $\text{CH}_3\cdot\text{CO}\cdot\text{CHEtPr}^\beta$, b. p. $154^\circ/760$ mm., a colourless liquid with a camphor-like odour, which on reduction with sodium in the presence of ether and water furnishes γ -isopropyl- β -pentanol, $\text{OH}\cdot\text{CHMe}\cdot\text{CHEtPr}^\beta$, b. p. $172^\circ/760$ mm., a colourless, oily liquid with an odour like that of sour bread. This substance is converted into β -iodo- γ -isopropylpentane,



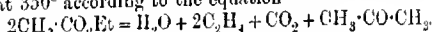
which on reduction yields β -methyl- γ -ethylpentane, identical with the product obtained by the preceding method.

β -Methyl- γ -ethylpentane (diethylisopropylmethane), $\text{CHMe}_2\cdot\text{CHEt}_2$, b. p. $114^\circ/760$ mm., is a nearly colourless liquid, with D_{20}^{25} 0.7084 and $[\alpha]_D^{25}$ 1.3996.

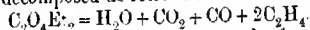
E. G.

Behaviour of Fats and Oils towards Calcium Carbonate. A. KÜNKLER and H. SCHWEDHELM (*Chem. Zentr.*, 1908, **4**, 1322; from *Seifensieder-Zeit.*, 1908, **35**, 165—166).—With the object of throwing light on the origin of petroleum and mineral waxes, the behaviour of fats, oils, waxes, and resins with chalk, common salt, and clay has been investigated. The results indicate the intermediate formation of a calcium salt and a ketone; the latter, especially in the presence of a contact substance like chalk, loses part of its oxygen, probably as water, at moderate temperatures, and as carbon monoxide or carbon dioxide at high temperatures. In these circumstances, it becomes possible to explain the optical activity and high viscosity of these natural oils by the carbon of the keto-group becoming asymmetric in the presence of mixed ketones, and by the formation of complex molecules with branching chains and having high viscosity. As explaining the fact that large quantities of carbon dioxide do not occur with natural oils, it is stated that the elimination of oxygen from the fatty acids only takes place on or near the surface of the earth. J. V. E.

Catalytic Dehydration of Organic Compounds. JEAN B. SENDERENS (*Compt. rend.*, 1908, **146**, 1211—1213. Compare this vol., ii, 166).—The author has extended his work on the dehydration of organic compounds by means of gently-calced alumina. At 300°, ethyl ether is decomposed into water and ethylene; this is a good method of preparation of the latter gas. Acetic acid at 350° gives acetone, water, and carbon dioxide. Propionic acid is similarly decomposed with formation of diethyl ketone. Ethyl acetate is acted on at 350° according to the equation



Ethyl oxalate is decomposed as follows:



Alumina can also effect the removal of 1 mol. of a halogen hydride; thus, at 250°, chloroisobutane yields isobutylene, chloropropane gives propylene, and ethylene dichloride at 350° furnishes vinyl chloride. Glycerol gives acetaldehyde and polyglycerols, and oxalic acid is completely transformed into water and carbon mon- and di-oxide. In all cases, heat alone has no action at the temperatures used. J. C. C.

Mixed Trihalogen Derivatives of Methane. VICTOR AUGER (*Compt. rend.*, 1908, **146**, 1037—1039).—In the preparation of dichloriodomethane by the action of mercuric chloride on iodoform (Serullas, *Ann. Chim. Phys.*, 1827, [ii], **34**, 97; Bouchardat, *Annalen*, 1837, **22**, 233), chlorodiiodomethane, HCl_2I , is also formed. Thus distillation under 100 mm. pressure of an intimate mixture of 700 grams of mercuric chloride and 1100 grams of iodoform gives 235 grams of pure dichloriodomethane, CHCl_2I , b. p. 40°/30 mm., 131°/760 mm., D₄ 2.41, and 323 grams of chlorodiiodomethane, CHClI_2 , a colourless liquid, m. p. -4°, b. p. 88°/30 mm., 200°/760 mm. (decomp.), D₄ 3.17, which is very unstable in the presence of air and light, becoming rapidly coloured violet. It is decomposed by water in the presence of air, giving carbonyl chloride and probably the compound COClI .

The product obtained by Bouchardat (*loc. cit.*) by the action of

bromine on iodoform was a mixture of bromoform and iodine (Löschner, *Abstr.*, 1888, 436), not, as this author thought, dibromiodomethane, CHBr_2 . The latter can be readily prepared by distilling under 150 mm. a mixture of equal parts of iodoform and mercuric bromide. *Dibromiodomethane*, CHBr_2 , is a white, crystalline solid, m. p. 22.5° , b. p. $101-104/50$ mm., $91\frac{1}{2}/42$ mm. In the solid state it is stable towards light, but its solutions are very unstable in the presence of air. Bromine converts it even at 0° into bromoform. In the preparation, *bromodi-iodomethane*, CHBrI , is also formed, but cannot be isolated in a pure state; it is readily prepared by the action of cold bromine on iodoform dissolved in carbon tetrachloride, when a mixture of the isomerides is formed which can be separated by fractional crystallisation. *Bromodi-iodomethane* forms yellow, hexagonal crystals, m. p. 60° , b. p. $110/25$ mm., unchanged by light when in the solid state, but very unstable in solution. E. H.

Catalytic Dehydration of Alcohols by Calcium Sulphate and by Aluminium Silicate. JEAN B. SENDERENS (*Bull. Soc. chim.*, 1908, [iv], 3, 633-638).—A continuation of work on the dehydration of alcohols by heated inorganic materials (compare *Abstr.*, 1907, ii, 218; i, 577; 1908, ii, 166). Gypsum, dehydrated by careful calcination, and also "plaster of Paris" begin to decompose ethyl alcohol at 370° and dehydrate it rapidly at 420° , yielding a gas containing over 90% of ethylene, the rest being hydrogen. Anhydrite does not decompose ethyl alcohol below 460° , and then only slowly, yielding a gas containing 85.7% of hydrogen and 14.3% ethylene. Gypsum, which has been calcined at a red heat during three hours, approaches anhydrite in its behaviour, acting on alcohol slowly at 485° , and yielding a gas containing 71.2% of hydrogen. These results are explained by assuming that the dehydration is due to the formation of temporary hydrates of the sulphate, and the tendency of the latter to form hydrates is diminished, probably as the result of change in molecular structure, either by heating at a high temperature during a short period or at a low temperature over a long period. In confirmation of this, it is pointed out that finely-powdered gypsum, not previously dehydrated, at first decomposes alcohol rapidly at $420-430^\circ$, and as the heating is continued, the rate falls to 17% of its initial value in the course of ten hours. Aluminium silicate, "modelling clay," and "white clay" also decompose alcohol rapidly at 420° , and, unlike calcium sulphate, their efficiency does not change as the result of their being previously calcined. The gas produced contains 94-98% of ethylene. Kaolin decomposes alcohol slowly at 370° , and more readily at 420° , yielding in the two cases gases containing 87% and 93.5% of ethylene respectively. After being calcined at a red heat, it approaches aluminium silicate and the clays mentioned above in efficiency. The presence of iron oxide or calcium carbonate in the clays modifies their action, and gives rise to a mixture of gases richer in hydrogen.

T. A. H.

Studies in Steam Distillation and the Recovery of Amyl Alcohol from the Acid Liquors obtained in the Gerber Process. H. DROOP RICHMOND (*Analyst*, 1908, 33, 209-217).—In

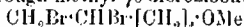
the first part of this paper the author deals* with steam distillation from a mathematical and theoretical point of view, whilst in the second part, the results of experiments on the recovery of amyl alcohol from the acid liquid obtained in the Gerber process of estimating fat in milk are described. It appears that a preliminary steam distillation of these liquids yields a crude amyl alcohol, which must be further purified by fractionation before a product boiling at $123-131^{\circ}$ is obtained which is suitable for use again in the Gerber process. The readings observed when this recovered amyl alcohol is employed show an excess of about 0.05%.

W. P. S.

Hydrate and Iodo-derivatives of Propargyl Alcohol (Propinol). ROBERT LESPIEAU (*Bull. Soc. chim.*, 1908, [iv], 3, 638-646).—An extension of previous work on propargyl alcohol and some of its derivatives (Abstr., 1898, i, 116; 1899, i, 184). In previous papers it was stated that this alcohol crystallises at -17° . The substance which separates in this way is a *monohydrate*, $C_3H_4O \cdot H_2O$. *Propargyl phenylurethane* crystallises from benzene on addition of light petroleum, and has m. p. $62-63^{\circ}$. Iodopropargyl alcohol, $HC \equiv CH_2 \cdot OH$, previously described (Abstr., 1899, i, 184), changes in part when kept or when treated with boiling water into tri-iodoallyl alcohol, $CI_3 \cdot CI \cdot CH_2 \cdot OH$, which is more readily obtained by adding iodine solution in slight excess to the copper derivative of propinol, suspended in potassium iodide solution and kept at 100° , and may be used for the characterisation of propargyl alcohol; *tri-iodoallyl acetate*, m. p. $41-41.5^{\circ}$, crystallises from acetic acid.

T. A. H.

Propargylcarbinol. ROBERT LESPIEAU and PARISELLE (*Compt. rend.*, 1908, 146, 1035-1037).—By passing a slow current of hydrogen bromide through methyl γ -dibromobutyl ether,



(Abstr., 1907, i, 580), kept at 100° until methyl bromide ceases to be evolved, cooling the product to 0° , saturating with hydrogen bromide, and heating in a sealed tube at 100° for ten hours, *$\alpha\beta$ -tri-bromobutane*, $CH_3Br \cdot CHBr \cdot [CH_2]_2 \cdot Br$, a liquid, b. p. $112-113/13$ mm., is formed. When this is heated to boiling with 20% by weight of solid potassium hydroxide, it is partly transformed into a *dibromobutylene*, b. p. $57-60^{\circ}/14$ mm., to which the authors ascribe the formula $CH_3 \cdot CBr \cdot [CH_2]_2 \cdot Br$.

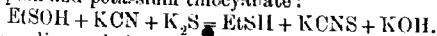
If the action of the potash is carried too far, acetylenic compounds are produced. *β -Bromo- Δ^a -butene- δ -ol*, $CH_3 \cdot CBr \cdot CH_2 \cdot CH_2 \cdot OH$, a liquid, b. p. $69-72^{\circ}/11$ mm., $175^{\circ}/760$ mm. (decomp.), is formed by the saponification of the corresponding *acelin*, a liquid, b. p. $75-78^{\circ}$, which results from the action of potassium acetate on *$\beta\delta$ -dibromo- Δ^a -butylene*. When *β -bromo- Δ^a -butene- δ -ol* is acted on by a 50% solution of potassium hydroxide, *butinol*, $CH_3 \cdot C \cdot CH_2 \cdot CH_2 \cdot OH$, a liquid, b. p. $133-136^{\circ}/760$ mm., is formed. This gives a *phenylurethane*, m. p. $66-67^{\circ}$. By treating butinol with an ammoniacal cuprous chloride solution, a yellow precipitate is formed, which, when suspended in a solution of iodine in potassium iodide and gradually heated at 100° , is converted into *$\alpha\beta$ -tri-iodo- Δ^a -butene- δ -ol*, $CI_3 \cdot CI \cdot CH_2 \cdot CH_2 \cdot OH$, a

substance, m. p. 112—113°, which becomes rose-coloured on exposure to light, and gives an *acetyl* derivative, m. p. 51—52°. E. H.

Alkylene Glycol-chlorohydrin Ethers and Tiffeneau's Wandering of Phenyl. PAUL HOERING (*Ber.*, 1908, 41, 1889—1893).—A reply to Houben (this vol., i, 307). G. Y.

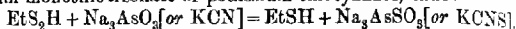
New Method for the Preparation of Diamyl Ether and Ethers of the Higher Alcohols. GEORG SCHROETER and WALTER SONDAG (*Ber.*, 1908, 41, 1921—1925. Compare Schroeter and Herzberg, *Abstr.*, 1905, i, 85; Kraft and Roos, *Abstr.*, 1892, 1219).—Large amounts of methyl ether are formed when methyl alcohol is heated with methionie acid at 120° under pressure, whilst ethyl ether and water distil continually when ethyl alcohol is run into a mixture of ethyl alcohol and methionie acid at 140°, the methionie acid being afterwards regained unchanged. Amyl and higher ethers are readily prepared by heating the corresponding alcohols with small amounts of methionie acid in an open vessel at about 40°. In this manner, amyl ether, b. p. 168—172°, can be obtained from commercial amyl alcohol in a 90—95% yield, taking into account the amount of alcohol regained. After fractionation over sodium, this amyl ether has b. p. 59·5—60°/10 mm. or 169·0—170·6°/760 mm., $\sigma_D + 0·187^\circ$. The commercial amyl alcohol had $\sigma_D - 1·03^\circ$ (compare Guye and Gantier, *Abstr.*, 1895, ii, 149, 195; Marekwald, *Abstr.*, 1904, i, 362). It is found, further, that benzenesulphonic acid and sulphuric acid can be employed in the same manner in the preparation of the higher ethers (compare Norton and Prescott, *Abstr.*, 1885, 496; Mamontoff, *J. Russ. Phys. Chem. Soc.*, 1897, 29, 230). The method of preparation can be employed only in the case of alcohols and ethers with b. p. above 130—140°, and of alcohols which have not too great a tendency to intramolecular fission of water. G. Y.

Action of Alkalis on Sodium Ethyl Thiosulphate. II. AUGUST GUTMANN (*Ber.*, 1908, 41, 1650—1655. Compare *Abstr.*, 1907, i, 671).—Sodium ethyl thio-sulphate when boiled with an alcoholic solution of potassium hydroxide is decomposed with the formation of sodium potassium sulphite, and not sulphate or thio-sulphate. Since analysis shows that 1 mol. of sulphite is produced from 1 mol. of sodium ethyl sulphite, the reaction which takes place may be represented thus: $\text{NaEtS}_2\text{O}_3 + \text{KOH} = \text{NaKSO}_3 + \text{EtSOH}$. The exact nature of the substance, EtSOH, which has not been isolated, is not yet known. It is converted by sodium arsenite in alcoholic sodium hydroxide solution, under pressure, into ethyl mercaptan and sodium arsenate: $\text{EtSOH} + \text{Na}_3\text{AsO}_3 = \text{EtSH} + \text{Na}_3\text{AsO}_4$, and by potassium cyanide and potassium sulphide in aqueous solution into ethyl mercaptan and potassium thiocyanate:



Similarly, sodium ethyl thio-sulphate is decomposed by an alcoholic solution of potassium hydrogen sulphide, yielding potassium sodium

sulphite and a substance, EtS_2H , thus: $\text{NaEtS}_2\text{O}_3 + \text{KSH} = \text{NaKSO}_3 + \text{EtS}_2\text{H}$. The alcoholic solution of the compound EtS_2H , when treated with sodium arsenite or potassium cyanide, yields ethyl mercaptan and sodium monothioarsenate or potassium thiocyanate, thus:



Attempts will be made to isolate the compound EtS_2H . W. H. G.

Hydrates of the Fatty Acids, according to Measurements of the Viscosity of their Solutions. D. E. TSAKALOTOS (*Compt. rend.*, 1908, 146, 1146—1149. Compare this vol., ii, 260; Dunstan, *Abstr.*, 1904, ii, 805).—The viscosities of aqueous solutions of formic, acetic, propionic, and *n*-butyric acids of different strengths have been measured at 20° by the Poiseuille-Ostwald method, the densities of the liquids being determined by means of a Sprengel-Ostwald pyknometer. The viscosity-coefficients (η) were calculated from the formula $\eta = k/dt$, where k is the constant of the apparatus, d the density of the solution, and t its time of flow. To determine k , an experiment was made with benzene, the value of η/d being found from Guye and Friderich's table. The results are given in tabular form. Whilst the viscosity of pure formic acid is greater than those of its homologues, the aqueous solutions of the latter are more viscous than those of formic acid. When the viscosities of the solutions are plotted against their concentrations, the curves obtained for acetic, propionic, and *n*-butyric acid exhibit well-defined maxima corresponding with concentrations of equal molecular quantities of acid and water, indicating the existence of the hydrates $\text{CH}_3\cdot\text{CO}_2\text{H}\cdot\text{H}_2\text{O}$, $\text{C}_2\text{H}_5\cdot\text{CO}_2\text{H}\cdot\text{H}_2\text{O}$, and $\text{C}_3\text{H}_7\cdot\text{CO}_2\text{H}\cdot\text{H}_2\text{O}$. The curve for formic acid, on the contrary, shows a regular decrease in viscosity from pure acid to pure water. *iso*-Butyric acid and water form two layers at concentrations between 20% and 50% of acid; the viscosities of the homogeneous solutions are higher than the values calculated by the rule of mixtures. E. H.

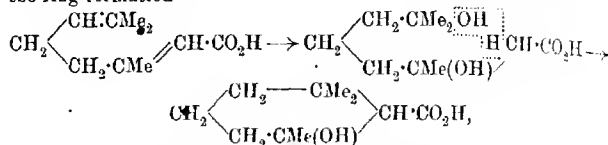
Action of Concentrated Sulphuric Acid on Glycerol Esters of Saturated Monobasic Fatty Acids. B. W. VAN ELDIK THIEME (*Proc. K. Akad. Wetensch. Amsterdam*, 1908, 855—860).—As is well known, the hydrolysis of esters is a reversible reaction: $\text{R}\cdot\text{CO}_2\text{R}' + \text{H}_2\text{O} \rightleftharpoons \text{R}\cdot\text{CO}_2\text{H} + \text{R}'\cdot\text{OH}$; the equilibrium between the reacting molecules is dependent on the temperature, the nature of the medium, and the nature of the ester. The velocity of the hydrolysis, which is low, is accelerated by hydrogen ions, but, so long as the amount of acid added is insufficient to modify markedly the nature of the medium, the equilibrium is unchanged. Hence the saponification of fats by dilute sulphuric acid cannot be carried to completion, but if concentrated sulphuric acid is employed, not only is the nature of the medium altered, but the reaction now takes place according to the equation: $\text{R}\cdot\text{CO}_2\text{R}' + \text{H}_2\text{SO}_4 \rightleftharpoons \text{R}\cdot\text{CO}_2\text{H} + \text{R}'\cdot\text{O}\cdot\text{SO}_3\text{H}$, and the equilibrium may be shifted completely to the right if the acid is anhydrous, if an excess of the acid is added to the dry fat, and if the temperature is maintained within certain limits. The following experiments show the influence of these three conditions on the saponification. Contrary to Bunte's statement (*Abstr.*, 1895, ii, 95), butter-fat cannot be

saponified completely by 93.5% sulphuric acid at 30–32°. It is found that at that temperature 81% of the butter-fat is hydrolysed by 93.5% sulphuric acid, 89.7% by 98.5% acid, and 92.2% by 100% acid. At 18°, 86.6% of trilaurin is saponified by 6.5 mols. of 100% sulphuric acid, 95.5% by 26 mols. of the same acid, and 100% by 52 mols. of the acid. If the mixture of sulphuric acid and completely saponified trilaurin is heated for one hour at 60°, 12.9% of trilaurin is again formed (compare Grün and Schacht, Abstr., 1907, i, 462). Lauric and sulphuric acids must form a molecular compound, as dry benzene extracts both acids from a mixture of trilaurin and 100% sulphuric acid (compare Hoogewerff and van Dorp, Abstr., 1899, i, 672; Meiger, *Monatsh.*, 1903, 24, 840). When heated with 52 mols. of 94.6% sulphuric acid, trilaurin yields 80% of lauric acid and 20% of mixed glycerides. It is considered that the mono- and di-laurins in this mixture are formed by the action of water on the compounds $C_{11}H_{23}\cdot CO\cdot O\cdot C_3H_7(O\cdot SO_3H)_2$ and $C_3H_7(O\cdot CO\cdot C_{11}H_{23})_2\cdot O\cdot SO_3H$. Grün and Schacht (*loc. cit.*) state that the action of sulphuric acid on glycerol leads to the formation of only glycerolmono- and glyceroldi-sulphuric acids. Experiments are now quoted showing that, on the contrary, the product of the action of 98.3% sulphuric acid is chiefly the tri- and di-sulphuric acids, only small amounts of glycerolmonosulphuric acid being formed, but that if the mixture is diluted with water the trisulphuric acid undergoes partial hydrolysis to the di- and mono-sulphuric acids (compare Claësson, Abstr., 1879, 1033).
G. Y.

Theory of the Saponification of the Glycerides. RUDOLF WEGSCHEIDER (*Monatsh.*, 1908, 29, 233–234).—Corrections of a few errors in a previous paper (this vol., ii, 165). W. H. G.

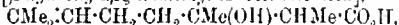
Theory of Saponification. IV. RICHARD FANTO and MILAN J. STRITAR (*Monatsh.*, 1908, 29, 299–316).—A continuation of the authors' investigation on the hydrolysis of fats (compare Abstr., 1907, i, 464).—The hydrolysis of tallow, beef-fat, tripalmitin, and olive-oil by solutions of potassium hydroxide in absolute, 95%, and 90% alcohol, sometimes in the presence of benzene, has been studied in the manner previously described (Abstr., 1904, i, 843; 1907, i, 277). The mixture of fats which is obtained on treating tripalmitin with an insufficient quantity of potassium hydroxide has also been investigated. The results obtained may be summarised as follows: (1) The hydrolysis of fats by aqueous potassium hydroxide (heterogeneous system) takes place directly. (2) The transformation of fats into ethyl esters under the influence of alcoholic potassium hydroxide solutions ("alcoholysis") in homogeneous systems proceeds throughout in separate stages. The same reaction also takes place in apparently heterogeneous systems; a perfect heterogeneous system cannot, however, be obtained with the constituents employed in studying this change, owing to the miscibility of the various substances produced by the esters. (3) The higher the percentage of water in the alcoholic potassium hydroxide solutions the closer does the course of the reaction approach to the direct hydrolysis of the true heterogeneous system. W. H. G.

Mechanism of the Ring Formations in the Geranic Series; Synthesis and Structure of Dihydromyrcene. MARC TIEFFENAU (*Compt. rend.*, 1908, 146, 1153—1155).—Tiemann (Abstr., 1898, i, 374) has explained the formation of isomeric cyclic compounds from derivatives of the geranic series by successive fixation and elimination of two molecules of water, although Barbier and Bouveault had shown (Abstr., 1897, i, 537) that, strictly, a single molecule was sufficient for the ring formation

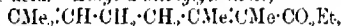


subsequent elimination of the second molecule of water being possible in two ways, thus giving rise to isomeric derivatives. To test the validity of this hypothesis, the author has studied the isomeric change of geranic compounds, in which the hydrogen atoms (one or both) combined with the carbon atom joined to the carboxyl group are substituted by alkyl groups.

When methylheptenone is condensed in the presence of zinc or magnesium with ethyl α -bromopropionate or ethyl or amyl α -chloropropionate, the ethyl or amyl ester of β -hydroxy- α -methyl- $\alpha\beta$ -dihydrogeranic acid [β -hydroxy- $\alpha\beta\gamma$ -trimethyl- Δ^8 -octenoic acid],



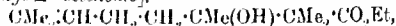
is formed. The ethyl ester has b. p. 145—146°/15 mm., D^{20}_D 0.9694; the amyl ester, 175—185°/14 mm. (decomp.), D^{20}_D 0.953. Each of these esters is transformed by acetyl chloride into the corresponding ester of α -methylgeranic acid. Ethyl α -methylgeranate,



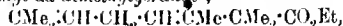
has b. p. 239—240°, D^{20}_D 0.9259; the amyl ester has b. p. 275—277°, D^{20}_D 0.9134. Both esters on saponification give α -methylgeranic acid, b. p. 156—158°/13 mm., D^{20}_D 0.961, which when distilled slowly at ordinary pressure loses carbon dioxide and forms Semmler's dihydromyrcene, $\text{CM}_2\text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CMe} \cdot \text{CHMe}$ (Abstr., 1901, i, 732), thus showing that the dehydration of the β -hydroxy- α -methyl- $\alpha\beta$ -dihydrogeranic acid is effected at the expense of the hydrogen combined with the neighbouring tertiary carbon atom.

α -Methylgeranic acid, but not its amyl ester, is transformed by sulphuric acid into a cyclic acid, b. p. 155—158°/11 mm., D^{20}_D 1.0071, which on distillation at ordinary pressure loses carbon dioxide, giving Semmler's cyclo dihydromyrcene (*loc. cit.*), $\text{CM}_2 \begin{array}{l} \text{CHMe} \cdot \text{CMe} \\ \text{CH}_2 - \text{CH}_2 \end{array} \text{CH}$, b. p. 168—170°/70 mm., D^{20}_D 0.8325, D^{18}_D 0.8217, n^{20}_D 1.460.

Condensation of methylheptenone with ethyl bromoisobutyrate gives ethyl β -hydroxy- $\alpha\alpha$ -dimethyl- $\alpha\beta$ -dihydrogeranate [ethyl β -hydroxy- $\alpha\alpha\beta\gamma$ -tetramethyl- Δ^8 -octenoate],



b. p. 160—163°/14 mm., D^{20}_D 0.9644, which on dehydration by acetyl chloride gives ethyl $\alpha\alpha$ -dimethylgeranate,



b. p. 248—251°, D₂₀ 0.9208, n_D 1.4609. The corresponding acid has b. p. 166—168°/15 mmf. The ester does not undergo ring formation when treated with sulphuric acid. E. H.

The Lactone of $\beta\gamma$ -Dihydroxybutyric Acid. P. CARRÉ (*Compt. rend.*, 1908, 146, 1282—1284. Compare Wagner, Abstr., 1894, i, 563).—When $\beta\gamma$ -dihydroxybutyric acid is distilled in a vacuum and the distillate fractionated, there are obtained at 92—93°/12 mm, the lactone of hydroxycrotonic acid (Lespieau, Abstr., 1904, i, 471) and the lactone of $\beta\gamma$ -dihydroxybutyric acid, $\begin{array}{c} \text{CH}_2-\text{CO} \\ | \quad \diagup \\ \text{CH}(\text{OH})\cdot\text{CH}_2 \end{array} > \text{O}$, b. p. 174—175°/12 mm. With alkalis, the acid is regenerated. The benzoyl derivative, $\begin{array}{c} \text{CH}_2-\text{CO} \\ | \quad \diagup \\ \text{CH}(\text{OBz})\cdot\text{CH}_2 \end{array} > \text{O}$, has m. p. 101°. J. C. C.

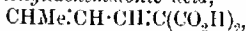
Condensation of Aldol and Crotonaldehyde with Malonic Acid. ADOLF RIEDEL (*Annalen*, 1908, 361, 89—95).—When heated with pyridine in a reflux apparatus, aldol and malonic acid condense, forming sorbic acid and anhydrohydroxydihydrosorbic acid. It is considered that the first product of the reaction is probably $\beta\delta$ -dihydroxybutylnalonic acid, $\text{OH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{CO}_2\text{H})_2$, which loses carbon dioxide and water, forming β -hydroxydihydrosorbic acid, $\text{CHMe}\cdot\text{CH}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, two molecules of this then forming the anhydro-acid.

Anhydrohydroxydihydrosorbic acid, $\text{C}_{12}\text{H}_{18}\text{O}_5$, is obtained as a viscid, yellow oil, which loses water, changing into sorbic acid, slowly at the ordinary temperature, but more rapidly when boiled with concentrated hydrochloric acid or when distilled in a vacuum. The silver,

$\text{C}_{12}\text{H}_{16}\text{O}_5\text{Ag}_2$, barium, $\text{C}_{12}\text{H}_{16}\text{O}_5\text{Ba}_2\cdot 4\text{H}_2\text{O}$, and copper, $\text{C}_{24}\text{H}_{30}\text{O}_{10}\text{Cu}_2$, salts decompose when heated, forming the corresponding sorbates.

When heated together in quinoline, aldol and malonic acid yield an acid, $\text{C}_{12}\text{H}_{16}\text{O}_4\cdot\text{H}_2\text{O}$, which is obtained as a resinous, reddish-yellow oil, and is considered to be a polymeric acid of sorbic acid. The silver, $(\text{C}_{12}\text{H}_{14}\text{O}_4\text{Ag})_2$, and copper, $(\text{C}_{12}\text{H}_{14}\text{O}_4\text{Cu})_2$, salts are described.

The action of crotonaldehyde on malonic acid in pyridine solution at the ordinary temperature leads to the formation of sorbic acid and small amounts of crotonylidenemalonic acid,



which separates from a mixture of benzene and light petroleum in yellow, granular crystals, m. p. 76°, and on further heating loses carbon dioxide, forming sorbic acid. G. Y.

The System Chloral-Water. C. VAN ROSSEM (*Zeitsch. physikal. Chem.*, 1908, 62, 681—712. Compare this vol., ii, 361).—The freezing points and boiling points of mixtures of chloral and water in various proportions have been determined. The pure chloral used had m. p. —57.5° and b. p. 97°/740 mm.

The form of the freezing-point curve indicates the existence of three compounds of chloral and water containing these components in the

molecular proportions 2:1, 1:1, and 1:7. The first of these is formed very slowly from the components, and undergoes a slow dissociation when fused. Its natural freezing point is about 43° , but the crystals may be heated rapidly to 80° without melting. The ordinary monohydrate, which occurs in two pseudo-symmetric modifications (compare Pope, *Trans.*, 1899, 455), also undergoes a slow dissociation when fused. Its natural freezing point is 47.4° , and the highest melting point observed was 54° . The heptahydrate is rapidly formed from the components, and has a constant melting point of -1.4° ; in this case there is no process of slow dissociation in the liquid phase.

When mixtures of chloral and water are boiled under a pressure of 740 mm., the composition of the vapour is for all concentrations only very slightly different from that of the liquid. When the boiling temperature is plotted against composition, a curve is obtained with a minimum and two points of inflexion. The boiling point of chloral hydrate is lower than that of either component, but does not coincide with the minimum on the boiling-point curve.

At the ordinary temperature, mixtures of chloral and water form two layers to begin with, but after a time become homogeneous, a considerable amount of heat being developed. At high temperatures (170° and above), homogeneous mixtures of chloral and water separate into two layers, the temperature of separation varying with the composition. The lowest temperature of separation observed was in the case of a mixture containing 60 molecular per cent. of chloral.

J. C. P.

Preparation of Methyl α -Chloropropyl Ketone. GEORG KORSCHUN (*Bull. Soc. chim.*, 1908, [iv], 3, 595–596. Compare Vladesco, *Abstr.*, 1891, 1183).—This chloro-ketone was prepared by a method already used for methyl α -chloroethyl ketone (*Abstr.*, 1905, i, 373), namely, the passage of a mixture of chlorine and carbon dioxide through methyl propyl ketone, cooled in a freezing mixture, and contained in a glass vessel connected to a second vessel containing distilled water. The passage of the two gases is continued until the increase in weight of the two vessels and their contents is equal to about 80% of the weight of ketone taken. The chloro-ketone is then isolated by fractional distillation, the portion having b. p. $63^{\circ} 95$ mm. being collected. The yield is 56.4 per cent.

T. A. H.

Acetylacetone Compounds of Metals of Group II. SEBASTIAN M. TANATAK and E. KEROVSKI (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 580–584).—In continuation of their work on the atomic weight of glucinum (*Abstr.*, 1907, i, 888; ii, 261), the authors have prepared the acetylacetone compounds of the metals of the second group in order to compare them with the corresponding glucinum compound. The only one of these compounds resembling that of glucinum is the zinc derivative. But whilst zinc and also cadmium readily form basic acetylacetone derivatives, no basic glucinum compound is formed even on boiling a solution of the normal acetylacetone compound with glucinum carbonate and oxide.

Magnesium acetylacetonate, $\text{Mg}(\text{CHAc}_2)_2$, forms long, white crystals and exhibits normal ebullioscopic behaviour in alcohol.

Calcium acetylacetonate, $\text{Ca}(\text{CHAc}_2)_2 \cdot 2\text{H}_2\text{O}$, forms white, acicular crystals.

Zinc acetylacetonate, $\text{Zn}(\text{CHAc}_2)_2$, forms yellow crystals, m. p. 130° ; can be distilled at a pressure of 350 mm., and has the normal molecular weight in boiling alcohol.

Strontium acetylacetonate, $\text{Sr}(\text{CHAc}_2)_2 \cdot 2\text{H}_2\text{O}$, is insoluble in any of the ordinary solvents.

Basic cadmium acetylacetonate, $\text{Cd}(\text{CHAc}_2)_2 \cdot \text{CdO}$, is amorphous; the normal salt could not be prepared.

Barium acetylacetonate, $\text{Ba}(\text{CHAc}_2)_2 \cdot 2\text{H}_2\text{O}$, crystallises in plates.

Mercuric acetylacetonate, $\text{Hg}(\text{CHAc}_2)_2$, forms white crystals.

T. H. P.

Application of Barfoed's Reagent to Show the Hydrolysis of Disaccharides by Enzymes. HERBERT E. ROAF (*Bio.-Chem. J.*, 1908, 3, 182—184).—The presence of lactase and maltase may be determined readily by the use of Barfoed's reagent, which when used with certain precautions is not reduced by disaccharides, but is reduced by the monosaccharides into which they are decomposed.

W. D. H.

The Properties of Starch in Relation to its Colloidal Condition. EUGÈNE FOUARD (*Compt. rend.*, 1908, 146, 978—981. Compare this vol., i, 138).—The physical properties of true "soluble starch," filtered through a membrane of collodion, have been further investigated.

The freezing-point depression is nil, so that soluble starch has no osmotic pressure. If the freezing-point depression be taken as less than 0.001° , the molecular weight must be more than 15,000, equivalent to a cluster of 45 molecules of maltose. This, however, is not the initial condition of the molecules, since the act of freezing brings about a slight opalescence of the solution.

Ultramicroscopic examination shows that the particles are much smaller than those in colloidal starch solution, soluble starch being, in fact, indistinguishable from many other true solutions.

Soluble starch may have $[\alpha]_D$ $183^\circ 15'$ to $191^\circ 50'$, according to the texture of the collodion filter employed. The greater the proportion of starch which passes through the filter the higher the specific rotatory power. The various collodion filters may be compared with a set of sieves of different mesh which sort out molecular aggregates of various sizes.

When a solution which passed entirely through the filter was evaporated down in a vacuum at 15° or in the drying oven at 60° , it would no longer pass through entirely. Dilution of this solution increased the amount which passed from 71.1% to 91.0% of the total starch present. Thus partial evaporation and subsequent dilution served to destroy the condition of perfect solubility of the starch. The author concludes that water itself is an essential factor in modifying the molecular aggregation of pure starch. The action is a reversible

hydrolysis in accordance with the law of mass action. Soluble starch molecules are not necessarily already formed in natural starch, but are more probably formed by the hydrolysing action of water on it. When a true solution of starch is allowed to age, it sets to a compact magma. This change is reversible, is accelerated by acids or low temperature, and retarded by alkalis or heat.

When a starch solution is converted into the granular condition, the conductivity increases from about 73.4×10^{-6} to a constant value of 226.7×10^{-6} . Since the solutions contain a very slight trace of a weak acid, perhaps an acid phosphate (compare Abstr., 1907, i, 391), the increase in conductivity is ascribed to the liberation of the molecules of this electrolyte which remain combined with the soluble starch until the latter is polymerised. When the above-mentioned maximum conductivity is reached, no further granulation occurs, although only a small fraction of the total starch has been coagulated.

A very important relationship must subsist between the organic starch molecule and its saline environment.

R. J. C.

Highly Nitrated Cellulose, Hydrocellulose, and Oxycellulose. ERNST BERL and R. KLAYE (*Chem. Zentr.*, 1908, i, 1381; from *Zeitsch. Schiess. Sprengstoffwesen*, 1907, 2, 381—387. Compare Abstr., 1907, i, 390).—With the object of ascertaining whether highly nitrated cellulose (13.5% N) is true cellulose nitrate, oxycellulose nitrate, hydrocellulose nitrate, or a mixture of these substances, nitration experiments have been carried out with cellulose, hydrocellulose, and oxycellulose under exactly similar conditions. The substances used were cellulose, hydrocellulose, hydracellulose, KMnO_4 -cellulose, Br oxycellulose, HNO_3 -oxycellulose, KClO_3 -oxycellulose, bleaching powder-oxycellulose, and a new oxycellulose prepared by the authors by means of calcium permanganate, all of which, besides being freed from fat, were analysed, microscopically examined, and tested with methylene-blue, Fehling's solution, &c. The results show that the product of nitrating pure cellulose at the ordinary temperature is pure cellulose ester; hydrocellulose and oxycellulose, under the same conditions, are not capable of being so highly nitrated as pure cellulose. The solubility of the nitrate from hydro- or oxy-cellulose in a mixture of ether and alcohol is the same as that of the product from pure cellulose which has the same nitrogen content. Hydro- and oxy-cellulose nitrate exhibit a greater attraction for methylene-blue than does the HNO_3 -ester of pure cellulose of identical nitrogen content. Cellulose, hydro- and oxy-cellulose have a greater attraction for methylene-blue than their nitric acid-esters. The viscosity of acetone solutions of nitrates of pure cellulose is considerably greater than that of similar solutions of the nitrates of hydro- and oxy-cellulose having the same nitrogen content and prepared at the same temperature.

J. V. E.

Gradual Nitration of Cellulose and Denitrification of Cellulose Nitrate by means of Acid Mixtures. ERNST BERL and R. KLAYE (*Chem. Zentr.*, 1908, i, 1381—1382; from *Zeitsch. Schiess. Sprengstoffwesen*, 1907, 2, 403—406).—It is shown that a cellulose

nitrate (13.86% N), prepared by means of nitrogen pentoxide, is stable when treated with hot water, so the cause of the esterification of cellulose by means of nitric and sulphuric acids not taking place to the theoretical extent (14.14% N) is not due to the instability of the product when containing more than 13.5% N. Rather is it to be ascribed to the sulphuric acid, which, besides favouring the nitration by removing water, has a tendency to hydrolyse the nitric acid-ester, as also have the H-ions of the nitric acid. Equilibrium is established between the ester formed and the acid, and it follows that for every acid mixture a definite cellulose nitrate should be produced. The validity of this explanation is shown by the examination of the product obtained from treating pure cellulose and three different cellulose nitrates with acid mixtures of various strengths, the time of action and the temperature being also varied.

J. V. E.

Cellulose Nitrates and Cellulose Acetonitrates. EANST BERL and WATSON SMITH, jun. (*Ber.*, 1908, 41, 1837—1844).—When treated with nitric acid and an excess of acetic anhydride, cellulose yields highly nitrated products; acetylation does not occur. Similar products are formed when Pictet and Khotinsky's acetyl nitrate (*Abstr.*, 1907, i, 175) is used. When, however, sulphuric acid is present, acetyl nitrates of cellulose are formed, probably owing to the sulphuric acid hydrolysing several of the nitrate groups and subsequent acetylation. The percentage of nitrogen in these mixed esters tends to increase as the proportion of acetic anhydride to the acid mixture is decreased. The nitrates obtained in the absence of sulphuric acid appear to be less soluble in concentrated sulphuric acid than the ordinary nitrates.

When the proportion of acetic anhydride is small, nitrates are not formed to any appreciable extent.

J. J. S.

A Laevorotatory Substance Found in Altered Beetroot. JULIUS WEISBERG (*Bull. Soc. chim.*, 1908, [iv], 3, 601—604; *Bull. Assoc. chim. Sucr. Dist.*, 1908, 25, 946—949*).—Examination of juice expressed from beetroot, which had become "frosted" and partly rotten, showed that it contains a laevorotatory substance, which is precipitated by lead subacetate solution and by milk of lime, and which on boiling with dilute mineral acids decomposes, forming dextrorotatory products (arabinose and dextrose?) which reduce Fehling's solution. The substance appears therefore to differ from Fremy's parapectic acid only in being laevorotatory in place of dextrorotatory, and it is proposed to call it *l*-parapectic acid. There is reason to believe that it is formed from the dextrorotatory pectous matter originally present in the roots.

T. A. H.

Double Phosphate of Magnesium and Methylamine. MAURICE FRANÇOIS (*Compt. rend.*, 1908, 146, 1284—1287).—The author has investigated Quantin's method (*Abstr.*, 1893, ii, 101) of separating ammonia from the methylamines, and finds that, contrary to Quantin's statement, monomethylamine is precipitated by magnesium phosphate, giving *magnesium methylamine phosphate*,

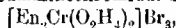
* and *Zeitsch. Ver. deut. Zuckerind.*, 1908, 595—598.

$\text{Mg}(\text{NH}_3\text{Me})\text{PO}_4 \cdot 6\text{H}_2\text{O}$. This is even exclusively formed when equal molecular quantities of ammonia, monomethylamine, and magnesium phosphate are mixed. The latter reagent does not precipitate solutions of di- or tri-methylamine. The conclusion is drawn, therefore, that Quantin's method cannot be applied to the separation of ammonia and monomethylamine, but only to the separation of mixtures of di- and tri-methylamine and ammonia.

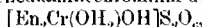
J. G. C.

Stereochemistry of Chromium. V. Stereoisomeric Aquo- and Hydroxy-salts. PAUL PFEIFFER [with R. PRADÉ and R. STERN] (*Zeitsch. anorg. Chem.*, 1908, 58, 228—256. Compare Abstr., 1907, i, 895; this vol., i, 79).—The preparation and properties of certain stereoisomeric aquo- and hydroxy-salts of chromium are described, including two new examples of structural isomerism.

cis-Dibisaquodiethylenediaminechromium bromide,

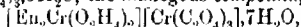


has already been described (*loc. cit.*). The corresponding *chloride*, $[\text{En}_2\text{Cr}(\text{O}_2\text{H}_4)_2]\text{Cl}_3$, prepared by the action of hydrochloric acid on *cis*-hydroxyaquadithylenediaminechromium dithionate,

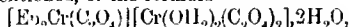


forms lustrous, orange-red plates. Both salts are considerably hydrolysed in aqueous solution, and from these, by the action of pyridine, the basic salts, $[\text{En}_2\text{Cr}(\text{O}_2\text{H}_4)\text{OH}]\text{X}_2$ ($\text{X} = \text{Cl}$ or Br), are obtained in claret-red crystals, soluble with neutral reaction in water. By the action of mineral acids on these salts, the dibisaquo-salts are regenerated, as represented by the equation $[\text{En}_2\text{Cr}(\text{O}_2\text{H}_4)_2]\text{X}_3 \rightleftharpoons [\text{En}_2\text{Cr}(\text{O}_2\text{H}_4)\text{OH}]\text{X}_2 + \text{HX} + \text{H}_2\text{O}$. By the action of potassium iodide and dithionate respectively on the hydroxy-salts, the corresponding *iodide*, $[\text{En}_2\text{Cr}(\text{O}_2\text{H}_4)\text{OH}]\text{I}_3$, lustrous, claret-red, compact crystals, and *dithionate*, $[\text{En}_2\text{Cr}(\text{OH}_2\text{OH})\text{S}_2\text{O}_6]$, small, claret-red needles, have been prepared; the latter contains a molecule of water less than the other salts.

By interaction of the *cis* dibisaquo-bromide, $[\text{En}_2\text{Cr}(\text{O}_2\text{H}_4)_2]\text{Br}_3$, and potassium chromium thiocyanate, $\text{K}_3\text{Cr}(\text{SCN})_6$, in dilute acetic acid solution, the compound, $[\text{En}_2\text{Cr}(\text{O}_2\text{H}_4)_2][\text{Cr}(\text{SCN})_6] \cdot \text{H}_2\text{O}$, is obtained as a red powder. From the same bromide and blue potassium chromium oxalate, $\text{K}_3\text{Cr}(\text{C}_2\text{O}_4)_3 \cdot 3\text{H}_2\text{O}$, the analogous compound,



is obtained in lustrous, violet-brown leaflets. A compound isomeric with the last-mentioned, of the formula



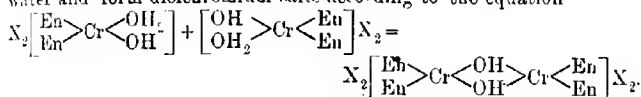
is obtained in small, lustrous, reddish-yellow crystals by interaction of the oxalato-chloride, $[\text{En}_2\text{Cr}(\text{C}_2\text{O}_4)]\text{Cl}$, and red potassium chromium oxalate, $[\text{Cr}(\text{OH})_2(\text{C}_2\text{O}_4)_2]\text{K} \cdot 4\text{H}_2\text{O}$, and subsequent addition of alcohol.

The *trans*-salts are prepared by methods analogous to those just described. The green *trans*-compound, $[\text{En}_2\text{CrBr}_2]\text{Br}$, is considerably hydrolysed in aqueous solution, and on adding potassium bromide and pyridine the basic salt, *trans*-hydroxyaquadithylenediaminechromium bromide, $[\text{En}_2\text{Cr}(\text{OH}_2\text{OH})\text{Br}_3]$, is obtained as lustrous, flesh-coloured leaflets. From the bromide by double decomposition, the corresponding *iodide* and *dithionate* have been prepared; both form flesh-

coloured crystals, and, like the bromide, dissolve in water with neutral reaction. By treating the bromide with hydrobromic acid (compare *cis*-series above), *trans*-dibisaquodithylenediaminechromium bromide, $[\text{En}_2\text{Cr}(\text{O}_2\text{H}_4)_2]\text{Br}_2$, is obtained in lustrous, prismatic, orange-brown needles; whether two of the water molecules are outside or inside the nucleus is not yet conclusively settled. On treatment with alcohol, or after keeping over phosphoric oxide for some time, the salt loses $2\text{H}_2\text{O}$, and *trans*-di aquodithylenediaminechromium bromide, $[\text{En}_2\text{Cr}(\text{OH}_2)_2]\text{Br}_2$, is obtained in orange-brown crystals. The *chloride*, *nitrate*, *thiocyanate*, and *oxalate* corresponding with the last-mentioned salt have also been prepared, but the last three salts have not yet been analysed. These salts are considerably hydrolysed in solution, the chief products being the *hydroxyaquo*-salts, $[\text{En}_2\text{Cr}(\text{OH}_2)(\text{OH})]\text{X}_2$, mentioned above as being obtainable by other methods.

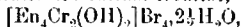
The properties of the corresponding compounds belonging to the *cis*- and *trans*-series are compared in detail. G. S.

Stereochemistry of Chromium. VI. Polynuclear Chromium Salts. PAUL PFEIFFER [with W. VORSTER and RICHARD STERN] (*Zeitsch. anorg. Chem.*, 1908, **58**, 272—296. Compare foregoing abstract).—When *cis*-hydroxyaquadithylenediaminechromium salts, or the corresponding hydroxybisaquo-salts, are heated, they lose water and form diolchromium salts according to the equation



The bromide of this series is obtained by the action of pyridine on the dilute aqueous solution of *cis*-dibisaquodithylenediaminechromium bromide, the hydroxybisaquo-salt being formed as intermediate product.

Tetraethylenediaminediolchromium bromide,



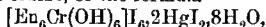
forms lustrous, bluish-violet crystals, soluble with neutral reaction in water; the bromine is precipitated quantitatively by silver nitrate. The salt is decomposed on heating with mineral acids; with concentrated hydrochloric acid the *cis*-dichloro-chloride, $[\text{En}_4\text{Cr}_2\text{Cl}_2]\text{Cl} \cdot \text{H}_2\text{O}$, is obtained, and with hydrochloric acid the *cis*-bromobisaquo-bromide,



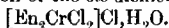
By double decomposition of the diolbromide with potassium iodide, the corresponding *iodide*, $[\text{En}_4\text{Cr}_2(\text{OH})_2]\text{I}_4 \cdot 2\frac{1}{2}\text{H}_2\text{O}$, is obtained in small, bluish-violet, lustrous needles.

A number of hexaethylenediaminehexoltetrachromium salts, which appear to have the general formula $\{\text{Cr}[\text{En}_2\text{Cr}(\text{OH})_2]_3\}\text{X}_6$, have been prepared as follows. Partly dehydrated chrome alum is heated for some time with ethylenediamine monohydrate, and the product is then treated with a little water and filtered; the residue is the crude sulphate of the series in question. When the sulphate is treated with hydrochloric acid in moderate excess, *hexaethylenediaminehexoltetrachromium chloride*, $[\text{En}_6\text{Cr}_4(\text{OH})_6]\text{Cl}_6 \cdot 6\text{H}_2\text{O}$, is obtained in small, red needles. From this salt by double decomposition, the corresponding

bromide and *iodide*, with $4\text{H}_2\text{O}$, *thiocyanate*, with H_2O , *dithionate*, with $7\text{H}_2\text{O}$, *nitrate*, with $6\text{H}_2\text{O}$, and *chromate*, with $5\text{H}_2\text{O}$, have been obtained; all occur in red needles except the chromate, which forms a brownish-red, apparently amorphous powder. A double salt of the iodide and mercuric iodide, of the formula



has also been obtained as a yellowish-red precipitate. These salts are slightly alkaline in reaction, do not unite with hydrochloric acid like the hydroxy-salts, and on heating with concentrated hydrochloric acid are decomposed with production of the *cis*-dichloro-chloride,



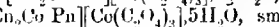
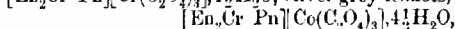
It is pointed out that these red hexol salts appear to be closely related to the rhodoso-salts of Jørgensen.

G. S.

Stereochemistry of Chromium. VII. Mixed Luteo-salts. PAUL PFEIFFER [with TH. GASSMANN and H. PIETSCH] (*Zeitsch. anorg. Chem.*, 1908, 58, 297—316. Compare foregoing abstracts).—As the isomerism persists when the nucleus halogen atoms in the *cis*- and *trans*-diacidodithylenediaminechromium (and cobalt) salts, $[\text{Eu}_2\text{CrX}_2]\text{X}$, are ionised by displacing them by water molecules (previous abstract, Part V), the question was investigated as to whether the *cis*-*trans*-isomerism also persists when a halogen in the nucleus is displaced by an ethylamine or propylamine group. This is found not to be the case, identical simple and mixed luteo-salts being obtained from the *cis*- and *trans*-compounds. The change of configuration takes place with the *trans*-compounds.

The salts were either prepared directly by heating the respective dichloro-chlorides, $[\text{Eu}_2\text{CrCl}_2]\text{Cl}$ and $[\text{Eu}_2\text{CoCl}_2]\text{Cl}$, with ethylenediamine and propylenediamine (Pn) respectively until the product became yellow, and then adding the alkali salt of the appropriate acid, or by double decomposition. *Diethylenediaminepropylenediaminechromium bromide*, $[\text{Eu}_2\text{Cr Pn}]\text{Br}_3 \cdot 2\text{H}_2\text{O}$, forms lustrous, yellow needles; the *iodide*, with $2\text{H}_2\text{O}$, and the *thiocyanate*, with $\frac{1}{2}\text{H}_2\text{O}$, also form lustrous, yellow needles. *Diethylenediaminepropylenediaminecobalt bromide* $[\text{Eu}_2\text{Co Pn}]\text{Br}_3 \cdot 3\text{H}_2\text{O}$, and the *iodide*, with $3\frac{1}{2}\text{H}_2\text{O}$, occur in brownish-yellow needles; the *thiocyanate*, with $\frac{1}{2}\text{H}_2\text{O}$, in small, yellow crystals. The solubility of the cobalt salts in water has been determined.

By interaction of the complex chromium and cobalt bromides just mentioned with potassium chromium oxalate and potassium cobalt oxalate respectively in aqueous solution, the four compounds,



green needles, $[\text{Eu}_2\text{Co Pn}][\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot 5\frac{1}{2}\text{H}_2\text{O}$, small green crystals, and $[\text{Eu}_2\text{Co Pn}][\text{Co}(\text{C}_2\text{O}_4)_3] \cdot 4\frac{1}{2}\text{H}_2\text{O}$, lustrous, silver-grey crystals, have been prepared. The compounds are decomposed into their components by heating with hydrochloric acid. By an analogous method, the four corresponding *cyanides* have been prepared, all of which occur in yellow crystals.

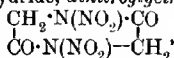
G. S.

Distillation of Esters of Amino-acids by means of the Geryk Pump. PHOEBUS A. LEVENE and D. D. VAN SLYKE (*Biochem. Zeitsch.*, 1908, 10, 214).—A sufficiently low pressure for the fractional

distillation of esters of amino-acids was obtained by the use of the Geryk pump, and the use of liquid air avoided, the vessel immersed in liquid air being replaced by one filled with cotton wool saturated with sulphuric acid and immersed in a freezing mixture.

W. D. H.

Nitration and Acetylation of Glycine Anhydride and its Methyl Homologues: Alanine Anhydride and α -Aminoisobutyric Anhydride. ANTOINE P. N. FRANCHIMONT and H. FRIEDMANN (*Rec. trav. chim.*, 1908, 27, 192—206. Compare Donk, Abstr., 1907, i, 331).—When glycine anhydride is added to a mixture of absolute nitric acid and acetic anhydride, *dinitroglycine anhydride*,



is obtained. This compound separates from ethyl acetate in large, glistening plates, which decompose at 145—146°. When dissolved in alcoholic ammonia, it furnishes nitroaminoacetamide, whilst sodium hydroxide converts it into the sodium salt of nitroaminoacetic acid.

Alanine anhydride dissolves in absolute nitric acid with formation of a *dinitrate*, which on treatment with acetic anhydride yields *dinitroalanine anhydride*, $\text{CHMe} \cdot \text{N}(\text{NO}_2) \cdot \text{CO} \cdot \text{N}(\text{NO}_2) \cdot \text{CHMe}$. This forms colourless needles decomposing at 136°.

Methyl α -aminoisobutyrate, $\text{C}_5\text{H}_{11}\text{O}_2\text{N}$, b. p. 136°/749 mm., D_4^{20} 0.9787, was prepared from α -aminoisobutyric acid; *hydrochloride*, decomp. 183°. When the ester is heated in a closed vessel for thirty-six hours at 230—240°, it forms *α -aminoisobutyric anhydride*, $\text{C}_5\text{H}_9\text{O}_2\text{N}$, which sublimes without melting. *α -Aminoisobutyramide*, $\text{C}_4\text{H}_9\text{O}_2\text{N}$, m. p. 127°, is very soluble in water, alcohol, and chloroform. *α -Nitroaminoisobutyric anhydride*, $\text{CMe}_2 \cdot \text{N}(\text{NO}_2) \cdot \text{CO} \cdot \text{NH} \cdot \text{CMe}_2$, crystallises from hot water in fine colourless needles, m. p. 166° (decomp.).

When treated with absolute nitric acid and acetic anhydride, this compound is transformed quantitatively into *dinitro- α -aminoisobutyric anhydride*, $\text{C}_5\text{H}_7\text{O}_6\text{N}_4$, rhombohedra, m. p. 108°, insoluble in water, but soluble in alcohol, ether, and benzene.

Diacetylglycine anhydride, $\text{C}_5\text{H}_{10}\text{O}_4\text{N}_2$, m. p. 102°, is very soluble in water and alcohol, and is readily prepared by dissolving glycine anhydride in acetic anhydride.

Diacetylalanine anhydride, $\text{C}_{10}\text{H}_{14}\text{O}_4\text{N}_2$, m. p. 132°, crystallises from hot water in shining needles. *α -Aminoisobutyric anhydride* is not attacked when boiled with acetic anhydride and sodium acetate, or with acetyl chloride.

W. O. W.

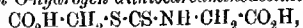
Derivatives of Dithiocarbaminoacetic Acid. H. KÖRNER (*Ber.*, 1908, 41, 1901—1905).—A study of the action of carbon disulphide on amino-acids.

A solution of *potassium dithiocarbaminoacetate* (*potassium glycine-N-dithiocarboxylate*), $\text{CS}_2\text{K} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{K}$, is obtained by the action of carbon disulphide on a solution of glycine in aqueous potassium hydroxide. The acid is unstable, and on liberation decomposes,

forming carbon disulphide. The potassium salt reacts easily with alkyl haloids, forming salts of the type $\text{CS}_2\text{R}\cdot\text{CH}_2\cdot\text{CO}_2\text{K}$, which on acidification yield stable, crystalline acids, $\text{CS}_2\text{R}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$. The *S*-ethyl *O*-hydrogen ester, $\text{CS}_2\text{Et}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, formed by shaking the potassium salt with ethyl bromide, crystallises in white prisms, m. p. 123—124°, and when treated with hydrogen chloride in ethyl-alcoholic solution yields the *ethyl* ester,

$\text{CS}_2\text{Et}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$,
crystallising in white needles; m. p. 72°. The *O*-methyl *S*-ethyl ester, $\text{CS}_2\text{Et}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$, has m. p. 75°.

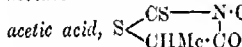
S-Carboxymethyl *O*-hydrogen dithiocarbaminoacetate,



prepared from the potassium salt and potassium chloroacetate, crystallises in white prisms, decomp. 80°, m. p. 120°, and changes when heated at 100°, or more slowly over sulphuric acid at the ordinary temperature, into *rhodaninacetic acid* (4-*keto*-2-*thio*thiazolidine-3-*acetic acid*), $\text{S}\cdot\text{CS}\cdot\text{N}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, which is formed also by the

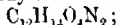
action of ethyl chloroacetate on potassium dithiocarbaminoacetate. It crystallises in yellow needles, m. p. 148°, and, when dissolved in hot water, again forms *S*-carboxymethyl *O*-hydrogen dithiocarbaminoacetate. *Ethyl rhodaninacetate*, $\text{C}_2\text{H}_5\text{O}_2\text{NS}_2$, crystallises in yellow needles, m. p. 58°. The *methyl* ester is obtained as a yellow oil which rapidly solidifies.

The action of a bromopropionic acid on potassium dithiocarbaminoacetate leads to the formation of 4-*keto*-2-*thio*-5-*methylthiazolidine*-3-*acetic acid*, $\text{S}\cdot\text{CS}\cdot\text{N}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$



G. Y.

Hydroxyprolines. HERMANN LEUCHS and HEINRICH FELSNER (*Ber.*, 1908, 41, 1726—1735).—The two synthetical hydroxyprolines (*Abstr.*, 1905, i, 545) when reduced with hydriodic acid and red phosphorus at 140—150° yield proline (pyrrolidine-2-carboxylic acid). Both acids combine with phenylcarbinide, yielding *derivatives*,



that from the α -acid crystallises from water in four-sided plates, m. p. 194—195° (corr., decomp.), and that from the β -acid forms six-sided plates, m. p. 187° (corr.). The phenylcarbinide derivatives readily yield *phenylhydantoins*, $\text{C}_{12}\text{H}_{12}\text{O}_2\text{N}_2$, when heated with dilute hydrochloric acid, these melt respectively at 164—165° (corr.) and 156—158° (corr.).

In order to determine whether one of the two artificial hydroxyprolines is the racemic form of the hydroxyproline obtained by hydrolysing gelatin, attempts have been made to racemise the natural product, but without success; the stability of this acid indicates that the hydroxy-group is in the β - or γ -position. Attempts to resolve the artificial acids did not meet with success.

δ -Chloro- α -bromovalerolactone reacts with aqueous methylamine, yielding a mixture of two hydroxyhygric acids. The two are readily separated by means of their copper salts, one of which is insoluble in alcohol.

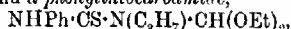
The δ - γ -hydroxy-*N*-methylproline (*hydroxyhygric acid*), $C_6H_{11}O_2N$, obtained from this insoluble copper salt is identical with the product obtained by methylating δ - γ -hydroxyproline. It crystallises from methyl alcohol in irregular polyhedra, m. p. 226—227° (corr.) (decomp.). The isomeric α - γ -hydroxy-*N*-methylproline crystallises in needles, m. p. 207—208° (corr.) (decomp.). J. J. S.

α -Amino-*n*-hexoic Acid [Leucine]. H. KUDIELKA (*Monatsh.*, 1908, 29, 351—358).—The author has prepared leucine by Fischer's method (Abstr., 1900, i, 646) from both natural and synthetical *n*-hexoic acids. Using Kahlbaum's preparations, 100 parts of the latter gave 37 parts of leucine, whilst 100 parts of the former gave only 6 parts. The copper salt, pale blue leaflets, nickel salt, greenish-blue salt, and cobalt salt, red leaflets, are described. The methylated base forms an *urichloride*, $C_6H_{19}O_2N \cdot HAuCl_4$, yellow leaflets, m. p. 142°. The solubilities of *d*- and *l*-leucine and of their copper salts in water are recorded. J. C. C.

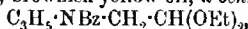
sec-Aminoacetals. CARL PAAL and LEO VAN GEMBEK (*Arch. Pharm.*, 1908, 246, 306—314).—The authors have prepared a number of *sec*-aminoacetals by the action of primary alkylamines on chloroacetal:



Tertiary bases are also formed in this reaction, which, however, were not investigated. The alkylaminoacetals are basic oils with an unpleasant odour, and are soluble in water. *n*-Propylaminoacetal, b. p. 185—192°, forms a *hydrochloride*, white, hygroscopic needles, m. p. 103—105°, a *hydrogen oxalate*, m. p. 175°, a *nitrosoamine*, viscid, yellow oil, and a *phenylthiocarbamide*,



white needles, m. p. 44—47°. *Allylaminoacetal*, b. p. 194—197°, forms a *hydrochloride*, m. p. 110—112°, a *hydrogen oxalate*, m. p. 175°, a *nitrosoamine*, a viscid, brownish-yellow oil, a *benzoyl* derivative,



viscid, yellow oil, a *phenylcarbamide*, yellow oil, and a *phenylthiocarbamide*, white, stellate needles, m. p. 81—82°. *n*-Butylaminoacetal, b. p. 207—210°, is a colourless, mobile liquid, of which the *hydrogen oxalate*, m. p. 190°, the *nitrosoamine*, brown, viscid oil, the *benzoyl* derivative, yellow, viscous oil, the *phenylcarbamide*, m. p. 50—52°, and the *phenylthiocarbamide*, m. p. 51—54°, were prepared. *isoAmylaminoacetal*, b. p. 215—220°, gives a *hydrochloride*, colourless plates, m. p. 33°, a *hydrogen oxalate*, m. p. 204°, a *nitrosoamine*, yellow oil; a *benzoyl* derivative, viscid oil, and a *phenylthiocarbamide*, m. p. 38—42°. J. C. C.

Properties of the Metallic Dithiocarbamates. MARCEL DELÉPINE (*Compt. rend.*, 1908, 146, 981—984; *Bull. Soc. chim.*, 1908, [iv], 3, 643—652. Compare Abstr., 1907, i, 594).—The author has prepared well-crystallised specimens representative of various types of dithiocarbamides, namely:

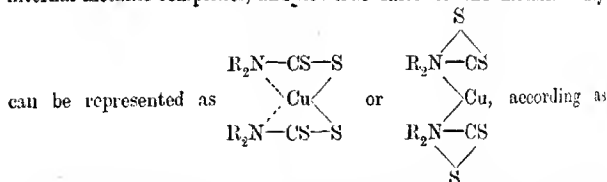
- I. $(\text{NH}_2 \cdot \text{CS}_2)_2\text{Ni}$ and $(\text{NH}_2 \cdot \text{CS}_2)_2\text{Co} \cdot 2\text{C}_3\text{H}_8\text{O}$ (acetone).
 II. $\text{NHPr} \cdot \text{CS}_2\text{Na} \cdot 4\text{H}_2\text{O}$, $\text{C}_4\text{H}_9 \cdot \text{NH} \cdot \text{CS}_2\text{Na} \cdot 4\text{H}_2\text{O}$, and $\text{NHPh} \cdot \text{CS}_2\text{Na} \cdot 3\text{H}_2\text{O}$.
 III. $(\text{C}_4\text{H}_9 \cdot \text{NH} \cdot \text{CS}_2)_2\text{Ba} \cdot 2\text{H}_2\text{O}$, $\text{NMe}_2 \cdot \text{CS}_2\text{Na} \cdot 2\frac{1}{2}\text{H}_2\text{O}$, and $\text{N}(\text{C}_4\text{H}_9)_2 \cdot \text{CS}_2\text{Na} \cdot 4\text{H}_2\text{O}$.
 IV. $\text{NHPr} \cdot \text{CS}_2\text{Cu}$; $(\text{C}_4\text{H}_9 \cdot \text{NH} \cdot \text{CS}_2)_2\text{Zn}$, and $(\text{NHPh} \cdot \text{CS}_2)_2\text{Co}$.
 V. $\text{N}(\text{C}_4\text{H}_9)_2 \cdot \text{CS}_2\text{Ag}$; $[\text{N}(\text{C}_4\text{H}_9)_2 \cdot \text{CS}_2]_2\text{Pb}$; $[\text{N}(\text{C}_4\text{H}_9)_2 \cdot \text{CS}_2]_2\text{Cu}$, and $[\text{N}(\text{C}_4\text{H}_9)_2 \cdot \text{CS}_2]_2\text{Ni}$.
 VI. $(\text{NMe}_2 \cdot \text{CS}_2)_2\text{Co} \cdot 2\text{CHCl}_3$; $[\text{N}(\text{C}_4\text{H}_9)_2 \cdot \text{CS}_2]_2\text{Co}$, and $[\text{N}(\text{C}_4\text{H}_9)_2 \cdot \text{CS}_2]_2\text{Fe}$.

The salts, which are often soluble in ether, chloroform, benzene, and carbon disulphide, have a tendency to crystallise with their solvent. Salts of alkali and alkaline-earth metals, also of zinc, are colourless; those of copper, nickel, cobalt, and iron are intensely and variously coloured, but without regard to the ordinary colours of these metals, in their salts. Ferrous and cobaltous salt could not be obtained, but, on the other hand, cupric salts rapidly and spontaneously change into cuprous salts. The salts $\text{NHPr} \cdot \text{CS}_2\text{Na}$ and $\text{NMe}_2 \cdot \text{CS}_2\text{Na}$ produce twice the theoretical freezing-point depression in aqueous solution.

In benzene or ethylene dibromide, the salts $[\text{NBu}_2 \cdot \text{CS}_2]_2\text{Ni}$ and $[\text{NBu}_2 \cdot \text{CS}_2]_2\text{Co}$ [$\text{Bu} = \text{C}_4\text{H}_9$], as also the ferric salt, give normal freezing-point depressions, showing that they correspond with the type RX_3 , and not with the type R_2X_2 .

The copper salt, $[\text{NBu}_2 \cdot \text{CS}_2]_2\text{Cu}$, gives a non-conducting solution in benzene, although the dry compound becomes electrified when pulverised. The absence of conductivity in solutions of these salts in moist organic solvents corresponds with a considerable indifference towards reagents. Thus copper is not precipitated by hydrogen sulphide, or nickel, cobalt, or iron by ammonium sulphide. $\text{NBu}_2 \cdot \text{CSAg}$ produces no precipitate even after ten minutes with hydrochloric acid. Lead, however, is easily precipitated from the dithiocarbamates by sulphuric acid or hydrogrogen sulphide.

The author contends that metallic dithiocarbamates are really internal metallic complexes, and not true salts of the metals. They



Warner's or Blomstrand and Jørgenson's notation is adopted. The alkali metals, which form true salts, can be replaced by copper present as oxide, and the copper dithiocarbamates are also stable in presence of sulphuric acid. Furthermore, several of the compounds are volatile; thus nickel and copper diisobutyldithiocarbamates distil unchanged in a vacuum.

R. J. C.

Hydrolysis of Aqueous Solutions of Ammonium Thiocyanate in Presence of Metallic Hydroxides. HERMANN GROSSMANN (*Zeitsch. anorg. Chem.*, 1908, 58, 265—271).—The freshly-

precipitated, well-washed hydroxides were boiled with a 10% aqueous solution of ammonium thiocyanate until no further change occurred. In these circumstances, the hydroxides of the alkalis and alkaline earths, including lithium and magnesium, decomposed the ammonium salt completely, the thiocyanates of the respective metals remaining in solution. With hydroxides of less basic character, there are three possible cases: (1) salts with complex cations are formed, for example, $\text{Zn}(\text{NH}_3)_2(\text{SCN})_2$ and $\text{Cu}(\text{NH}_3)_2(\text{SCN})_2$; (2) salts with complex anions are formed, for example, $\text{NH}_4[\text{Ag}(\text{SCN})_2]$ and $(\text{NH}_4)_2[\text{Co}(\text{SCN})_4] \cdot 4\text{H}_2\text{O}$; (3) both complex cations and anions may be formed. As examples of the last class, the compounds $\text{Hg}_2\text{ONH}_2(\text{SCN})_2$ and $(\text{NH}_4)_2\text{Hg}(\text{SCN})_4$

(Fleischer, 1875), as well as the cadmium compounds, $\text{Cd}(\text{NH}_3)(\text{SCN})_{22}$, $\text{Cd}(\text{NH}_3)_2(\text{SCN})_{21}$, and $(\text{NH}_4)_2\text{Cd}(\text{SCN})_{41} \cdot 2\text{H}_2\text{O}$, are already known, and by slightly modified methods the compounds $\text{Ni}(\text{NH}_3)_3(\text{SCN})_3$, bluish-green crystals, and $\text{Ni}(\text{NH}_3)_4(\text{SCN})_2$, dark blue crystals, have been prepared.

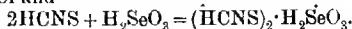
Hydroxides of very slight basic character, such as those of glucinum, aluminium, iron (ferric), and chromium, have practically no action on ammonium thiocyanate at boiling temperature. G. S.

[Hexathiocyano-salts of Molybdenum.] JOHANNA MAAS and JULIUS SAND (*Ber.*, 1908, 41, 1861).—A correction. It has been found possible to prepare the characteristic yellow zinc salt of the hexathiocyano-series as follows: an excess of ammonium thiocyanate is added to a solution of the green molybdenum trichloride containing hydrochloric acid, and kept at the ordinary temperature for twelve hours, air being excluded; the resulting liquid is then rendered ammoniacal, and finally treated with an ammoniacal solution of zinc chloride.

Since the yellow salts are formed in the absence of air, they must be aquo-salts having the general formula $\text{Mo}(\text{SCN})_6(\text{OH})_3\text{R}_3$, and not compounds of the type $\text{Mo}(\text{SCN})_6(\text{OH})\text{R}_3$ as stated previously (this vol., i, 397). W. H. G.

Thiocyanoselenious Acid: New Method for Estimating Selenium. W. I. IWANOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 661—664).—*Thiocyanoselenious acid*, $(\text{HCNS})_2 \cdot \text{H}_2\text{SeO}_3$, is formed by the interaction of a thiocyanate and selenious acid in presence of hydrochloric acid, the reactions being expressed by the equations:

$$\text{NH}_4\text{CNS} + \text{HCl} = \text{HCNS} + \text{NH}_4\text{Cl}$$
and



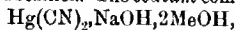
It separates as a voluminous precipitate, composed of pyramidal crystals. By heating or by the action of water, alcohol, glycerol, acid, or alkali, it decomposes with precipitation of red selenium. When treated with benzene or carbon disulphide, it dissolves partly, giving a yellow solution, which, on shaking with water, yields a colloidal selenium solution having at first a rose-red, and later a purple, colour. Nitric acid dissolves and oxidises it into selenious and sulphuric acids.

Attempts to prepare an analogous tellurium compound were unsuccessful.

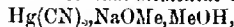
The instability of thiocyanoselenious acid affords a ready means of estimating selenium. To a solution containing from 0.1 to 0.4 gram of selenium, and diluted to about 600 c.c. with water, are added 20–30 c.c. of ammonium or potassium thiocyanate solution, and, after thorough stirring, about 150 c.c. of 25% hydrochloric acid. After being heated on a water-bath for twelve hours, the solution is filtered through a filter previously dried at 105° and weighed, the amorphous selenium on the filter being well washed with hot water, dried at 105°, and weighed. The precipitate often contains a small proportion of sulphur, which may be estimated by oxidising the precipitate in a glass or porcelain beaker with aqua regia, evaporating with hydrochloric acid to expel the nitric acid, dissolving the residue in hydrochloric acid and hot water, filtering, and precipitating with barium chloride. This method gives much better results than washing the precipitate with carbon disulphide, as in some cases part of the selenium is dissolved by this solvent, whilst in others, both sulphur and selenium remain undissolved.

T. H. P.

Compounds of Mercuric Cyanide with Alkalis and Nitric Acid. KARL A. HOFMANN and H. WAGNER (*Ber.*, 1908, 41, 1628–1634. Compare this vol., i, 143).—Mercuric cyanide solution decolorises a solution of phenolphthalein made alkaline with a little sodium hydroxide; this result cannot be due to hydrolysis, as only concentrated solutions of alkali precipitate oxide or basic salt, and from the agreement amongst themselves of the constants, determined by means of the solubility, depression of freezing point, conductivity, and hydrolysis of ethyl acetate, the conclusion is arrived at, that in dilute solutions the complex ion $\text{Hg}(\text{CN})_2 \cdot \text{OH}$ is present. Hexagonal crystals having the composition $\text{Hg}(\text{CN})_2 \cdot \text{KOH} \cdot 1\frac{1}{2} \text{H}_2\text{O}$ have been obtained from a solution of 13 grams of mercuric cyanide, 40 grams of potassium hydroxide, and 60 c.c. of water. An aqueous solution of this salt gives crystals of mercuric cyanide on concentration. Oxidising agents, such as hydrogen peroxide, precipitate mercury, and the aqueous solution gives silver cyanide with silver nitrate, mercury acetylido with acetylene, and cyanate with permanganate, showing that this solution is much more reactive than mercuric cyanide solution. The corresponding sodium compound, $\text{Hg}(\text{CN})_2 \cdot \text{NaOH} \cdot 1\frac{1}{2} \text{H}_2\text{O}$, forms long prisms, which in a vacuum over phosphoric oxide lose $\frac{1}{2}$ mol. of water. When the operations are carried out in alcoholic instead of aqueous solution, analogous alcohol compounds are obtained. The sodium compound,



forms hexagonal, doubling refracting prisms, which lose 1 mol. of methyl alcohol in a vacuum over phosphoric oxide; the potassium compound is similar, and the sodium methoxide derivative,



forms rectangular prisms and is stable in a vacuum, but decomposes in the light.

A hot solution of mercuric cyanide and 68% nitric acid deposits on cooling the compound, $\text{Hg}(\text{CN})_2 \cdot \text{HNO}_3$, which crystallises in needles. It is explosive, and the strongly acid aqueous solution does not give precipitates with either ammonia or alkali, a distinction from the double salt, $\text{Hg}(\text{CN})_2 \cdot \text{AgNO}_3$.

W. R.

Constitution of Certain Mercuric Salts with Complex Cations. VINCENZO BORELLI (*Gazzetta*, 1908, 38, i, 361—426).—

The author has studied the reactions, cryoscopic behaviour, electrical conductivity, and transport numbers of the complex salts which mercuric cyanide forms with the strongly dissociated mercuric perchlorate and nitrate, and with the feebly dissociated mercuric chloride and acetate. The results indicate that all these complex salts are constitutionally analogous, and all contain the same cation, HgCN' . They are hence to be regarded as salts of "cyanomercury" having the constitutions $\text{HgCN}\cdot\text{ClO}_4$, $\text{HgCN}\cdot\text{NO}_3$, $\text{HgCN}\cdot\text{Cl}$, and $\text{HgCN}\cdot\text{OAc}$, since they all dissociate according to the scheme $(\text{HgCN})\text{A} \rightleftharpoons \text{HgCN}' + \text{A}'$. The complex cyanomercury ion, HgCN' , is very stable in all these compounds, and its dissociation according to the equation $\text{HgCN}' \rightleftharpoons \text{Hg}'' + \text{CN}'$ is extremely small in amount. Further, a study of mercuric oxycyanide indicates that its properties are expressed, not by the formula $\text{Hg}(\text{CN})_2\cdot\text{HgO}$, but by $\text{O}(\text{HgCN})_2$, so that it is really cyanomercury oxide, which yields the corresponding hydroxide when dissolved in water. In concentrated, but not in dilute, aqueous solutions, cyanomercury perchlorate, nitrate, and chloride give a precipitate of mercuric oxide on the addition of sodium hydroxide solution, whilst cyanomercury acetate gives a precipitate of cyanomercury oxide under similar conditions. Solutions which are not precipitated by sodium hydroxide give a precipitate with ammonia solution, whilst still more dilute solutions are precipitated only by hydrogen sulphide. With silver nitrate, solutions of the perchlorate, nitrate, or acetate give no precipitate, whilst the chloride gives a precipitate consisting entirely of silver chloride; the concentration of the cyanogen ions is, hence, very small in all cases.

Cyanomercury perchlorate, $(\text{HgCN})\text{ClO}_4$, obtained by evaporating a concentrated aqueous solution of mercuric perchlorate (1 mol.) and mercuric cyanide (1 mol.) in a vacuum over sulphuric acid at the ordinary temperature, forms white, acicular prisms, soluble in water or alcohol. In solution it undergoes gradual reduction, with partial formation of mercurous salt. Cryoscopic determinations show that it is dissociated to the extent of 0.80, 0.83, and 0.97 in solutions containing 1.05, and 0.2 mol. respectively per litre. The conductivity in aqueous solution increases considerably with the dilution ($\Lambda_{1024} = 349.9$; $\Lambda_{32} = 174.4$), the dissociation being of the same order of magnitude as that occurring in solutions of mercuric perchlorate ($\Lambda_{1024} = 296.9$; $\Lambda_{32} = 126.9$). The transport number of the cation HgCN' with respect to the anion ClO_4' in solutions of medium concentration (0.2 mol. per litre) and at about 20° is about 0.338.

Cyanomercury nitrate, $(\text{HgCN})\text{NO}_3$, chloride, $(\text{HgCN})\text{Cl}$, and acetate, $(\text{HgCN})\text{C}_2\text{H}_3\text{O}_2$ (compare Prussia, *Abstr.*, 1899, i, 318), exhibit behaviour in general similar to that of the perchlorate. The transport number of the cation HgCN' with respect to the anion NO_3' in solutions of medium concentration at the ordinary temperature is about 0.323. Examination of the products of electrolysis of the chloride in aqueous solution shows that the ion $(\text{HgCN})'$ may give rise to two other ions, namely, the cyanic ion, $(\text{CNO})'$, at the anode and the cyanogen ion, $(\text{CN})'$, at the cathode; the former of these is

probably formed by the addition of an atom of oxygen to the cyanogen ions existing in small quantity near the electrode, and the latter by the dissociation of the cyanomercury ion.

That cyanomercury oxide (compare Richard, *J. Pharm. Chim.*, 1903, 18, 553) forms the corresponding hydroxide, $(\text{HgCN})\text{OH}$, in solution is shown by cryoscopic and ebullioscopic measurements. The solution has a conductivity of the same order of magnitude as that of mercuric cyanido, so that the compound is dissociated to only a slight extent.

T. H. P.

Experiments to Obtain Aliphatic Substituted Oxytriazines and Oxydihydrotriazines. HEINRICH BILTZ [With P. HORRMANN] (*Ber.*, 1908, 41, 1880—1886).—An account of fruitless attempts to prepare oxytriazines and oxydihydrotriazines of the aliphatic series by methods employed with success in preparing similar aromatic compounds (compare Biltz, *Abstr.*, 1905, i, 491, 673). The work of Diels *Abstr.*, 1902, i, 205; 1903, i, 862), carried out with the same object, has been confirmed.

Diacetyl monosemicarbazone dissolves in aqueous sodium hydroxide without forming an oxytriazine derivative. The sodium salt, $\text{C}_6\text{H}_8\text{O}_2\text{N}_3\text{Na}$, crystallises in nodular aggregates. A mixture of diacetyldioxime and dimethylacetyleneurein (compare Franchimont and Klobbie, *Abstr.*, 1889, 125) is obtained by treating an alcoholic solution of carbamide and diacetyloxime with a few drops of concentrated sulphuric acid.

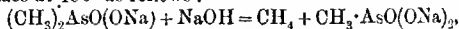
Diacetyloximesemicarbazone, $\text{C}_6\text{H}_{10}\text{O}_2\text{N}_3$, prepared by treating diacetyl oxime with semicarbazido hydrochloride and sodium acetate, has m. p. 247° (decomp.); with a short thermometer, m. p. $259-260^\circ$ (decomp.); the acetate crystallises in aggregates of needles, m. p. 216° .

Dimethylketolsemicarbazone, $\text{OH}\cdot\text{CHMe}\cdot\text{CMe}\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, obtained by acting on dimethylketol with semicarbazide hydrochloride and sodium acetate, has m. p. $194-195^\circ$ (short thermometer). The solution in concentrated sulphuric acid when carefully diluted yields a substance, m. p. about 270° (decomp.), which is probably diacetyldisemicarbazone. Dimethylketolsemicarbazone decomposes at 200° , yielding a yellow, vitreous mass.

W. H. G.

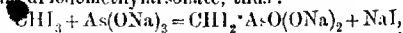
Action of Alkalis on Mono- and Di-methylarsonic Acids and their Iodo-derivatives. VICTOR AUGER (*Compt. rend.*, 1908, 146, 1280—1282).—When sodium methylarsonate is heated with excess of sodium hydroxide at $250-280^\circ$, it is decomposed according to the equation: $\text{CH}_3\cdot\text{AsO}(\text{ONa})_2 + \text{NaOH} = \text{CH}_4 + \text{AsO}(\text{ONa})_2$.

Sodium cacodylate undergoes a similar decomposition, the first stage taking place at 180° as follows:



the sodium methylarsonate then being decomposed at 260° according to the preceding equation.

The fact that methylene iodide is formed by the action of trisodium arsenite on iodoform is explained by assuming the intermediate formation of sodium di-iodomethylarsonate, thus:



which then decomposes into methylene iodide and sodium arsenate (this vol., i, 13). Details are given for the preparation of methylene iodide by this method.

J. C. C.

Conversion of *cyclopentene* into the Mono- and Di-aldehydes of Glutaric Acid. CARL D. HARRIES and LUDWIG TANK (*Ber.*, 1908, 41, 1701—1711).—In a future communication, the authors will give a comparison of the stability of different ring systems, based on the rate of decomposition of ozonides by water. The present paper deals with *cyclopentene*, the ozonide of which is readily decomposed by water, whilst that of *cyclohexene* is only decomposed with difficulty, although the stability of the two ring systems should be of the same order according to the tension theory of Baeyer.

It is very probable that only those aliphatic compounds which contain two carbonyl groups in the β -position to one another are capable of existing in the enolic form, since such compounds are very rarely obtained by the decomposition of ozonides, the substance in its enolic form undergoing further oxidation. *cyclopentene*, b. p. 45—46°, D_4^{20} 0.7754, n_D^{20} 1.42080, obtained by the distillation of *cyclopentanol* with phosphoric oxide, yields when ozonised in excess of cold hexane a viscous *ozonide*, $C_5H_8O_3$, which has the usual odour and properties of such compounds. It is rapidly attacked by boiling water, yielding hydrogen peroxide, glutaric acid, glutardialdehyde, and γ -aldehydobutyric acid.

Glutardialdehyde, $CHO \cdot [CH_2]_3 \cdot CHO$, b. p. 71—72°/10 mm. or 187—189°/760 mm., is a colourless, mobile liquid, which resembles succindialdehyde in many respects (this vol., i, 133). In the presence of a trace of water, it changes into a "glassy" polymeride, which reverts to the unimolecular form by distillation in a vacuum. It has D_4^{20} 1.1238 and n_D^{20} 1.45523, and the molecular refraction indicates that the substance is a true dialdehyde. The *bisnitrophenylhydrazones* has m. p. 79—80°.

γ -*Aldehydobutyric acid*, $CHO \cdot [CH_2]_3 \cdot CO_2H$, b. p. 240°/760 mm. or 136—138°/9 mm., is a viscous liquid with a strongly acid reaction, which reduces ammoniacal silver and Fehling's solutions, is resinified by sodium hydroxide, and very readily oxidises to glutaric acid. It has $D_4^{18.5}$ 1.1657, $n_D^{18.5}$ 1.44973, and the molecular refraction indicates that the substance is a true aldehyde. The high dielectric constant, 23.86 (aniline = 7.2), indicates that the aldehydic character is more pronounced than the acid. The *oxime* has m. p. 110—111°, or, after repeated crystallisation from water, 107—108°. The *semicarbazone* has m. p. 165—166° (decomp.), and the *nitrophenylhydrazones*, 148.5°. The analyses of these three compounds are not very accurate.

cycloheptene, D_4^{20} 0.823, n_D^{20} 1.45301, ozonised in carbon tetrachloride, yields a viscous, and in some cases a solid, *ozonide*, the analyses of which give numbers between $C_7H_{12}O_3$ and $C_7H_{12}O_4$. The ozonide is decomposed only slowly by boiling water, but the amount is too small to allow of the identification of the products. C. S.

Addition of the Higher Oxides to Doubly Unsaturated Hydrocarbons. A New Case of Addition in the 1:4 Position. HEINRICH WIELAND and HANS STENZL (*Annalen*, 1908, 380, 299—322).—As the evidence in favour of Thiele's theory of conjugated linkings has consisted so far chiefly in the addition of hydrogen, bromine, and

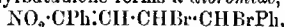
hydrohaloids, it seemed of importance to study the behaviour of conjugated linkings towards other addenda. Moreover, the investigation of the positions assumed by the group NO_2 on addition to conjugated ethylene linkings, offered some points of interest in connexion with previous studies on the form in which the higher oxides of nitrogen combine with unsaturated compounds (Abstr., 1904, i, 54, 415, 596; 1905, i, 706). The authors have therefore investigated the constitution of the compounds formed by addition of NO_2 groups to $\alpha\delta$ -diphenylbutadiene, $\text{CHPh}:\text{CH}:\text{CH}:\text{CHPh}$ (compare this vol., i, 35), cyclopentadiene, $\text{CH}_2\text{CH}=\text{CHCH}=\text{CH}_2$, and dicyclopentadiene,

the constitution of which has not as yet been established.

The following new evidence is brought forward in favour of the formulation of the additive compound of $\alpha\delta$ -diphenylbutadiene and nitric peroxide as $\alpha\delta$ -dinitro- $\alpha\delta$ -diphenyl- Δ^2 -butylene.

On reduction with the usual reagents and in the ordinary way, the dinitro-compound forms $\alpha\delta$ -diphenylbutadiene, a reaction further exemplifying the analogy of the behaviour of the nitro-group with that of the halogens, but, on reduction with zinc and hydrochloric acid under special conditions, it yields small amounts of *diphenylbutadienediamine*, $\text{NH}_2\text{CHPh}:\text{CH}:\text{CH}:\text{CHPhNH}_2$, which crystallises in colourless needles, m. p. 149° (decomp.), decolorises permanganate in acid solution, and when treated with nitrous acid evolves nitrogen and yields an oil. The diamine forms colourless, crystalline salts with acetic and hydrochloric acids, and a *picrate*, $\text{C}_{16}\text{H}_{18}\text{N}_2 \cdot 2\text{C}_6\text{H}_3\text{O}_7\text{N}_3$, yellow needles, decomp. about 220° . When suspended in chloroform, cooled by ice, and oxidised with ozone, the dinitro-compound yields large amounts of nitrophenylmethane, $\text{CH}_3\text{Ph}\cdot\text{NO}_2$, the decomposition product of nitrophenylacetic acid, $\text{NO}_2\text{CHPh}\cdot\text{CO}_2\text{H}$, together with small amounts of benzoic acid and benzaldehyde, arising probably from the intermediate formation of α -nitro- $\alpha\delta$ -diphenylbutadiene. If the additive compound was $\alpha\beta$ -dinitro- $\alpha\delta$ -diphenyl- Δ^2 -butylene, oxidation would lead to the formation of a dinitro-carboxylic acid, $\text{NO}_2\text{CHPh}\cdot\text{CH}(\text{NO}_2)\cdot\text{CO}_2\text{H}$.

α -Nitro- $\alpha\delta$ -diphenylbutadiene forms a *dibromide*,



which crystallises in yellow needles, m. p. 106° , decomp. about 165° , and gives a cherry-red coloration with concentrated sulphuric acid.

When suspended in cooled ether and treated with nitrous gas, α -phenylcinnamylacrylic acid, $\text{CHPh}:\text{CH}:\text{CH}:\text{CPh}\cdot\text{CO}_2\text{H}$, evolves carbon dioxide and yields a *dinitro* compound, which is probably $\beta\gamma$ -*dinitro- $\alpha\delta$ -diphenylbutadiene*, $\text{CHPh}:\text{C}(\text{NO}_2):\text{C}(\text{NO}_2):\text{CHPh}$; this crystallises in yellow prisms, m. p. 218° , is stable towards acids or cold alkalis, and does not form an additive compound with bromine.

The bearing of these facts on the nature of the ethylene linkings in diphenylbutadiene is discussed. It is considered that the partial



formula.

valencies of the α - and δ -carbon atoms are neutralised by those of the benzene rings, the behaviour of the compound being best expressed by the annexed

The action of nitrogen trioxide on *cyclopentadiene* in ethereal solution leads to the formation of a ψ -nitrosite,

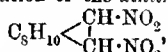


which is obtained in yellow crystals, m. p. 38° , decomposes slightly above its m. p., readily polymerises, gives Liebermann's reaction, and is converted by amyl nitrite and alcoholic hydrogen chloride into the

nitrosochloride, $(\text{N}_2\text{O}_2) \left[\text{CH} \begin{array}{c} \text{CH}_2 - \text{CH} \\ \text{CHCl} - \text{CH} \end{array} \right]_2$; this crystallises in colourless

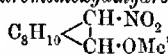
needles, detonates at about 142° , decolorises permanganate, forms potassium chloride with potassium hydroxide in methyl-alcoholic solution, and gives an orange coloration with phenol and concentrated sulphuric acid.

The action of nitrogen dioxide on *dicyclopentadiene* in ethereal solution leads to the formation of the *dinitro*-compound,



which crystallises in needles, m. p. 122° , is readily attacked by permanganate, does not give Liebermann's reaction, forms a crystalline *dibromide*, and loses 1 mol. of hydrogen nitrite when boiled with alcohol, or alcoholic potassium hydroxide or ammonia.

The ψ -nitrosite, $(\text{N}_2\text{O}_2) \left[\text{CH} \begin{array}{c} \text{CH} \cdot \text{NO}_2 \\ \text{C}_8\text{H}_{10} \end{array} \right]_2$, formed by the action of nitrogen trioxide on *dicyclopentadiene*, crystallises in hexagonal leaflets, m. p. 144 – 146° (decomp.), forms green solutions, reacts slowly with permanganate, does not give Liebermann's reaction, and when boiled with potassium in methyl-alcoholic solution evolves nitrous oxide and forms *nitromethoxydihydrodicyclopentadiene*,



which crystallises in rhombohedra, m. p. 68° , gives a blood-red coloration with alcoholic ferric chloride, forms *precipitates* with zinc, silver, and copper salts in neutral solution, and reacts slowly with

permanganate. The *nitro-oxime*, $\text{C}_8\text{H}_{10} \begin{array}{c} \text{CH} \cdot \text{NO}_2 \\ \text{C} \cdot \text{NOH} \end{array}$, formed by boiling

the ψ -nitrosite with alcohol or aniline in alcoholic solution, crystallises from benzene in prisms or needles, m. p. 138 – 139° , gives an intense green coloration with ferric chloride, and yields hydroxylamine when boiled with 20% sulphuric acid. G. Y.

Compounds of Platinous Chloride with *Dicyclopentadiene*.

KARL A. HOFMANN and J. VON NARRUTT (*Ber.*, 1908, 41, 1625–1628).—It has been already found that mercuric chloride, *dicyclopentadiene*, and alcohols give compounds of the class $\text{HgCl} \cdot \text{C}_{10}\text{H}_{12} \cdot \text{OR}$ (Hofmann and Seiler, *Abstr.*, 1906, i, 786), and it has since been discovered that platinous chloride in aqueous alcohols reacts in a similar way to form the stable ethers, $\text{PtCl} \cdot \text{C}_{10}\text{H}_{12} \cdot \text{OR}$.

Chloroplatomethoxydicyclopentadiene, $\text{PtCl} \cdot \text{C}_{10}\text{H}_{12} \cdot \text{OMe}$, obtained by mixing an aqueous solution of potassium platinichloride with a methyl-

alcoholic solution of dicyclopentadiene, crystallises in pale yellow plates, decomp. 190° . At 15° , the experiment requires several weeks; at 40° , several days. Hot potassium hydroxide decomposes it into hydrocarbon, and 20% hydrochloric acid at 15° slowly converts the plates into prisms, probably the compound $\text{PtCl}\cdot\text{C}_{10}\text{H}_{12}\text{Cl}$. The *ethoxy*-compound, $\text{PtCl}\cdot\text{C}_{10}\text{H}_{12}\cdot\text{OEt}$, forms pale yellow prisms; propyl alcohol does not give an analogous compound, but the compound, $\text{PtCl}\cdot\text{C}_{10}\text{H}_{12}\text{Cl}$, which separates in needle aggregates. The conclusion is drawn that these compounds owe their stability partly to their containing the linking $\text{ClPt}\cdot\overset{|}{\underset{|}{\text{CH}}}\cdot\overset{|}{\underset{|}{\text{CH}}}\cdot\text{Cl}$ or OMe . W. R.

The Optical Behaviour of cycloHexadiene Derivatives. KARL AUWERS (*Ber.*, 1908, 41, 1828—1831. Compare Abstr., 1906, i, 347; Brühl, *Trans.*, 1907, 91, 115).—The author draws attention to the fact that many cyclohexadienes which contain conjugated ethylene linkings do not show the exaltation in molecular refraction and dispersion usually characteristic of such compounds. It is pointed out that many of these unsaturated hydrocarbons tend to polymerise, and that determinations should be made with freshly-prepared specimens, the low values obtained for some of the compounds may possibly be due to the fact that polymerised products were examined.

Methyl 1:4-dimethyl- $\Delta^{1:3}$ -hexadiene-2-carboxylate also does not exhibit the usual exaltation. J. J. S.

Dihydrotoluene ($\Delta^{1:3}$ -Methylcyclohexadiene). CARL D. HARRIES (*Ber.*, 1908, 41, 1698—1701).—The dihydrotoluene obtained by the dry distillation of hexahydro-*m*-tolylenediamine phosphate (Abstr., 1901, i, 194; 1902, i, 361) yields by suitable oxidation with potassium permanganate the same 1:2-dihydroxymethylcyclohexane-3-one as is obtained from methylcyclohexenone (Abstr., 1898, i, 402), and is consequently $\Delta^{1:3}$ -methylcyclohexadiene. Klages found, however (Abstr., 1907, i, 597), that the observed and calculated molecular refractions agreed, although it is well known that substances containing a conjugated double linking exhibit an exaltation of this constant. The author has therefore redetermined the physical constants of this dihydrotoluene, and, with D_4^{20} 0.8354 and n_D^{20} 1.47628, the observed molecular refraction, 31.72, shows a small increment over the calculated value, 31.43. This result points to the presence in the dihydrotoluene of an isomeride which does not contain a conjugated double linking. Evidence in the same direction is obtained by the action of bromine, more than one molecular proportion of the halogen being absorbed. The action of ozone on dihydrotoluene gives a gelatinous product, which is apparently a mixture of a mono- and a di-ozonide, but the decomposition of the substance by water does not give conclusive results as to its structure. C. S.

Contact Oxidation of Hydrocarbons. E. I. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 652—658. Compare this vol., i, 306).—The author has investigated the oxidation of various hydrocarbons under the conditions of the former experiments (*loc. cit.*).

With light petroleum, D 0.71, the gaseous products of oxidation

included 8—10% of carbon dioxide and 6·8—2·4% of carbon monoxide, other products being about 10% of close-chain and ethylene hydrocarbons of the compositions C_6H_{12} and C_5H_{10} . Further aldehydic derivatives of the benzene series with the aldehyde group in the meta- or para-position were also obtained. Heavier oils yield similar products.

Benzene yields (1) a gaseous product containing 12·44% of carbon dioxide, 2·44% of oxygen, 6·78% of carbon monoxide, 6·94% of methane, and 71·4% of nitrogen; (2) aldehydic and carboxylic derivatives of benzene. From a study of the various products, the author concludes that the benzene undergoes a series of condensations and oxidations; for instance, $2C_6H_6 = H_2 + C_6H_5 \cdot C_6H_5$ (the latter being then oxidised to "acroleinphenol," benzaldehyde, and a hydroxybenzoic acid) and $3C_6H_6 = 2H_2 + C_6H_5 \cdot C_6H_4 \cdot C_6H_5$, the latter being then transformed into hydroxydiphenylcarboxylic acid or the corresponding aldehyde.

Toluene yields, in addition to the gaseous products, 2·5—4% of benzaldehyde and various substances with reducing and phenolic properties, and similar to the corresponding products obtained from benzene.

In the case of turpentine, the gas obtained has the following composition: CO_2 , 7·55%; O, 1·77%; CO, 7·55%; H, 4·8%; CH_4 , 3·6%; C_2H_4 , 1·2%; N, 73·5%. The other products obtained indicate that the turpentine loses part of its hydrogen and condenses to hydrocarbons of the diphenyl series, the latter then undergoing oxidation as in the case of benzene (*vide supra*).

The results so far obtained indicate that many gases, for example, natural methane and illuminating gas, may be converted by contact oxidation into more valuable products, such as formaldehyde.

T. H. P.

1:2-Dibromo-3-nitrobenzene and the Nitration of o-Dibromobenzene. ARNOLD F. HOLLEMAN [with P. C. J. EUWES] (*Rec. trav. chim.*, 1908, 27, 153—161. Compare Abstr., 1906, i, 345).—An improved method for the preparation of 1:2-dibromo-3-nitrobenzene from o-nitroaniline is described.

The m. p. previously ascribed to this compound (*loc cit.*) is too low. When crystallised from light petroleum, it has m. p. 84—85°. Pure o-dibromobenzene, m. p. 5·6°, has been treated at 0° with nitric acid (D 15). By an examination of the solidifying point and density, the product of nitration is found to consist of 84% 1:2-dibromo-4-nitrobenzene with 16% 1:2-dibromo-3-nitrobenzene. These two isomerides cannot be separated by fractional crystallisation. W. O. W.

Halogen Derivatives of Dinitrohydrocarbons. GIACOMO PONZIO and G. CHARRIER (*Atti R. Accad. Sci. Torino*, 1908, 43, 475—482; *Gazzetta*, 1908, 38, i, 648—654).—Whereas two forms of ω nitrotoluene are known having the structures $CH_3Ph \cdot NO_2$ and $CHPh \cdot NO \cdot OH$ respectively, only one form of ω -dinitrotoluene, $CHPh(NO_2)_2$,

has been obtained (compare Ponzio, Abstr., 1906, i, 735; and Hantzsch, Abstr., 1906, i, 500); two potassium salts of ω -dinitrotoluene are, however, known, one colourless and probably having the structure $NO_2 \cdot CPh \cdot NO \cdot OK$, and the other yellow and capable

of being represented by two formulæ, $\text{OK} \cdot \text{N} \cdot \text{CPh} \cdot \text{O} \cdot \text{NO}_2$ and $\text{OK} \cdot \text{CPh}(\text{NO}_2) \cdot \text{NO}$. The nature of the product of the action of hypochlorites on the yellow salt is in favour of the latter structure, a chlorine derivative being obtained which probably has the constitution $\text{NO} \cdot \text{CPh}(\text{NO}_2) \cdot \text{OCl}$, as it gives with alcoholic potash, potassium nitrate, nitrite, and benzoate in addition to the potassium salt of ω -dinitrotoluene. The alternative formula $\text{CPhCl}(\text{NO}_2)_2$ does not so well explain the facts. The yellow diazobenzene derivative obtained by the action of diazobenzene acetate on the yellow potassium salt of ω -dinitrotoluene is therefore probably $\text{NO} \cdot \text{CPh}(\text{NO}_2) \cdot \text{O} \cdot \text{N} \cdot \text{NPh}$, a formula which is in good accord with the easy transformation of the substance into nitronitrosobenzoylphenylhydrazine, $\text{NO}_2 \cdot \text{NBz} \cdot \text{NPh} \cdot \text{NO}$ (compare this vol., i, 482).

ω -Chlorodinitrotoluene, $\text{CPhCl}_2\text{NO}_2$, separates immediately on adding a dilute solution of potassium ω -dinitrotoluene to an alkaline solution of chlorine at 0° as a colourless oil which is stable under ordinary conditions; when warmed with water, it gives benzoic acid and nitrous fumes.

ω -Bromodinitrotoluene, obtained similarly, is a slightly yellow oil. The phenylhydrazine salt, $\text{CHPhN}_2\text{O}_4 \cdot \text{PhN}_2\text{H}_3$, of ω -dinitrotoluene, obtained by mixing aqueous solutions of potassium ω -dinitrotoluene and phenylhydrazine hydrochloride, forms yellow leaflets, m. p. 87° .

ω -Chlorodinitroanisole, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CClNO}_2$, and ω -bromodinitroanisole, prepared from ω -dinitroanisole, are colourless oils, which are stable at the ordinary temperature and give anisic acid when boiled with water; alcoholic potash converts both substances into potassium ω -dinitroanisole. The phenylhydrazine salt of ω -dinitroanisole forms yellow leaflets, m. p. 79° .

ω -Chlorodinitro-3:4-methylenedioxytoluene, $\text{CH}_2\text{O}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CClNO}_2$, prepared from ω -dinitro-3:4-methylenedioxytoluene, crystallises from alcohol in large, slightly yellow plates, m. p. 55° ; ω -bromodinitro-3:4-methylenedioxytoluene, m. p. 81° , crystallises from light petroleum.

W. A. D.

Reduction of Nitro-compounds by Zinin's Method. RICHARD WILLSTÄTTER and HEINRICH KUBLI (*Ber.*, 1908, 41, 1936—1940).—The authors find that when aromatic nitro-compounds are treated in alcoholic solution with ammonium sulphide in the cold, good yields of the corresponding aryl-hydroxylamines are obtained. From nitrobenzene was prepared phenylhydroxylamine; from *p*-nitrotoluene, *p*-tolylhydroxylamine, and α -nitronaphthalene gave α -naphthylhydroxylamine.

The latter crystallises with H_2O , forming colourless, glistening prisms, m. p. 79° (compare Scheiber, *Abstr.*, 1904, i, 867). The anhydrous substance has the same m. p. When α -naphthylhydroxylamine is dissolved in anhydrous ether and shaken with dry silver oxide in presence of anhydrous copper sulphate or sodium sulphate, it yields α -nitrosonephthalene in clear yellow crystals dissolving to a green solution. When heated, α -nitrosonephthalene turns green at 80° , and has m. p. 85 — 86° ; it then solidifies, and has m. p. 98° . J. C. C.

Picrates. WILHELM SUIDA (*Ber.*, 1908, 41, 1909—1913).—Anthranilic acid forms two picrates, $C_7H_7O_2N, C_6H_3O_7N_3$, yellowish-brown prisms, and $2C_7H_7O_2N, C_6H_3O_7N_3$, red, or when containing $1\frac{1}{2}H_2O$ yellow, crystals, depending on the proportions in which concentrated solutions of anthranilic and picric acids are mixed. In the same manner, *p*-toluidine and picric acid combine in the molecular proportion 1:1, forming a brownish-yellow, or in the proportion 2:1, forming a bright yellow, salt.

α -Naphthylamine also forms a greenish-yellow picrate containing 1 mol., and a copper-red picrate containing 2 mols., of the base and 1 mol. of picric acid. Aniline, on the other hand, forms only one brownish-yellow picrate. G. Y.

Tri-*p*-halogen Substitution Products of Triphenylmethane and Triphenylcarbinol. FRANS M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1908, 789—798. Compare Abstr., 1907, i, 1050).—Crystallographical determinations with the following substances: tri-*p*-iodotriphenylmethane, rhombic [$a:b:c=0.5765:1:0.8798$]; tri-*p*-iodotriphenylmethane containing benzene of crystallisation, triclinic [$a:b:c=0.5719:1:1.4298$; $\alpha=109^\circ 8'$; $\beta=126^\circ 21'$; $\gamma=107^\circ 32'$]; tri-*p*-chlorotriphenylcarbinol, rhombic [$a:b:c=0.6009:1:0.9781$]; tri-*p*-bromotriphenylcarbinol, rhombic [$a:b:c=0.8407:1:0.8081$]; tri-*p*-iodotriphenylcarbinol, rhombic [$a:b:c=0.8543:1:0.817$], and tri-*p*-iodotriphenylcarbinol containing benzene of crystallisation, triclinic [$a:b:c=1.3991:1:1.6135$; $\alpha=109^\circ 16'$; $\beta=117^\circ 36'$; $\gamma=62^\circ 52'$]. G. Y.

Mercury Salts of the Three Nitroanilines. C. LORING JACKSON and R. W. PEAKES (*Amer. Chem. J.*, 1908, 39, 567—572).—During a study of the abnormal replacement of bromine by hydrogen in 1:3:5-tribromo-2:4-dinitrobenzene, this substance was treated with the nitroanilines, but reaction did not take place under any conditions. The mercury salts of the nitroanilines were therefore prepared with a view to ascertaining if they would react with 1:3:5-tribromo-2:4-dinitrobenzene, but they gave no better results.

These salts, $(NO_2.C_6H_4.NH)_2Hg$, are precipitated when a strong solution of potassium hydroxide is added to a solution of the nitroaniline and mercuric nitrate. The salt of *p*-nitroaniline is crimson, that of the *m*-derivative is maroon-coloured and contains $1H_2O$, and that of the *o*-compound is bright red. The *o*-salt is formed the most rapidly, the *m*-salt next, and the *p*-salt most slowly. E. G.

Action of Bromine or of Sodium Hypobromite on *m*-Nitroaniline and Some of its Halogen Substitution Derivatives. WILHELM KÖRNER and ANGELO CONTARDI (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 465—480).—The authors have studied the action of bromine or sodium hypobromite on *m*-nitroaniline and some of its halogenated derivatives with the hope of obtaining new mono- and di-substituted derivatives of *m*-nitroaniline, and of ascertaining in what

order the three hydrogen atoms of *m*-nitroaniline, capable of substitution, are replaced by the halogen.

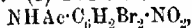
Bromination of *m*-nitroaniline with bromine in chloroform solution yields tribromo-*m*-nitroanilino, m. p. 102.5°, *p*-bromo-*m*-nitroaniline, and a small quantity of 2:4-dibromo-5-nitroaniline (*vide infra*).

Bromination of *m*-nitroaniline (1 mol.) with sodium hypobromite (1 atom of bromine) in acetic acid solution gives (1) 4-bromo-3-nitroacetanilide; (2) 2-bromo-5-nitroacetanilide, $\text{NHAc} \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{NO}_2$, which crystallises from alcohol in slender, monoclinic needles or prisms [ARTINI: $a:b:c = 3.3702:1:1.2522$; $\beta = 77^\circ 3'$], m. p. 180°, D 1.831. When treated with concentrated sulphuric acid at 120°, it is converted into 2-bromo-5-nitroaniline, $\text{NH}_2 \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{NO}_2$, which crystallises from alcohol in orange-yellow needles, m. p. 141°.

The action of sodium hypobromite on *p*-bromo-*m*-nitroaniline in acetic acid solution yields: (1) 2:4-dibromo-5-nitroacetanilide,



which crystallises from ethyl acetate in flattened needles or long plates, m. p. 172°, and can also be obtained, mixed with 2:4-dibromo-6-nitroacetanilide, by nitrating 2:4-dibromoacetanilide in sulphuric acid. De-acetylation of this compound yields 2:4-dibromo-5-nitroaniline, $\text{NH}_2 \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{NO}_2$, which crystallises from alcohol in slender, pale yellow, monoclinic laminae [ARTINI: $a:b:c = 2.1598:1:3.0212$; $\beta = 73^\circ 51'$], m. p. 114.2°. (2) 2:4-Dibromo-3-nitroacetanilide,

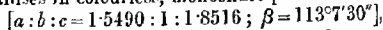


which crystallises from benzene in slender, white needles, m. p. 150°. When treated with nitrous acid, it is converted into 1:3-dibromo-2-nitrobenzene, which may be prepared conveniently in this way.

When 1:3-dibromo-2-nitrobenzene is treated with nitric acid, D 1.54, it yields 1:3-dibromo-2:4-dinitrobenzene, $\text{C}_6\text{H}_2\text{Br}_2(\text{NO}_2)_2$, which crystallises from alcohol in long, almost colourless needles or in yellowish-green plates, m. p. 83°, and, under the action of alcoholic ammonia solution, is converted into 2:4-dinitrophenylene-1:3-diamine, $\text{C}_6\text{H}_3(\text{NH}_2)_2(\text{NO}_2)_2$, which crystallises from alcohol in orange-yellow needles, m. p. 250°. When treated with potassium hydroxide solution, the latter yields the potassium salt of 2:4-dinitroresorcinol, $\text{C}_6\text{H}_2(\text{OK})_2(\text{NO}_2)_2$.

Nitration of 1:3-dibromo-2-nitrobenzene with excess of nitric acid, or with a mixture of nitric and sulphuric acids, results in the formation of 1:3-dibromo-2:4:6-trinitrobenzene, which, when treated with alcoholic ammonia solution, yields 2:4:6-trinitrophenylene-1:3-diamine (compare Noelting and Collin, Abstr., 1884, 1004). The latter, under the action of dilute potassium hydroxide solution, gives potassium styphnate.

Reduction of 1:3-dibromo-2-nitrobenzene with tin and hydrochloric acid, and replacement of the amino-group of the resultant product by bromine, leads to the formation of 1:2:3-tribromobenzene, $\text{C}_6\text{H}_3\text{Br}_3$, which crystallises in colourless, monoclinic plates

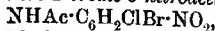


m. p. 87.4°, D 2.658. 2-Chloro-1:3-dibromobenzene, $\text{C}_6\text{H}_3\text{ClBr}_2$, obtained in a similar manner, m. p. 73°, and 2-iodo-1:3-dibromobenzene, $\text{C}_6\text{H}_3\text{Br}_2\text{I}$, m. p. 99.8°, crystallise in forms similar to that of the

tribromo-derivative. 2:6-Dibromoacetanilide, $C_6H_3Br_2 \cdot NHAc$, crystallises from alcohol in colourless, trimetric prisms
 $[a:b:c=0.734:1:0.392]$,

m. p. 210° , D_{16} 1.923.

The action of sodium hypobromite on *p*-chloro-*m*-nitroaniline in acetic acid yields (1) 4-chloro-2-bromo-5-nitroacetanilide,



which crystallises from alcohol in long, white needles, m. p. 147.4° , and is also obtained by nitrating 4-chloro-2-bromoacetanilide in sulphuric acid solution. The corresponding 4-chloro-2-bromo-5-nitroaniline, $NH_2 \cdot C_6H_2ClBr \cdot NO_2$, crystallises from alcohol in yellow, monoclinic prisms $[a:b:c=2.1321:1:3.0222; \beta=73^\circ 17']$, m. p. 108° , D 1.739. Replacement of the amino-group in this compound by hydrogen gives 1-chloro-3-bromo-6-nitrobenzene, m. p. 42.4° (compare Körner, this Journ., 1876, i, 204). (2) 4-Chloro-2-bromo-3-nitroacetanilide, $NHAc \cdot C_6H_2ClBr \cdot NO_2$, which crystallises from aqueous alcohol in colourless plates or faintly yellow prisms, m. p. $135-136^\circ$. The corresponding 4-chloro-2-bromo-3-nitroaniline, $NH_2 \cdot C_6H_2ClBr \cdot NO_2$, m. p. $99-100^\circ$, is similar in crystalline habit and chemical properties to the analogous dibromonitroaniline.

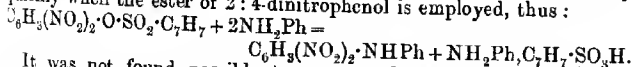
2-Bromo-5-nitroaniline is converted quantitatively into 2:4-dibromo-5-nitroaniline on bromination.

These results show that, in the bromination of *m*-nitroaniline, the positions accessible to the halogen are the para-position and, in a less degree, the ortho-position non-adjacent to the nitro-group; in no case does the halogen enter the meta-position. When the para-position in *m*-nitroaniline is already occupied by a halogen atom, the new halogen atom assumes indifferently either of the two ortho-positions. If the ortho-position is occupied, the halogen atom assumes the para-position.

Partial bromination of 3:5-dinitroaniline yields (1) 2-bromo-3:5-dinitroaniline, $NH_2 \cdot C_6H_2Br(NO_2)_2$, which crystallises from alcohol in golden-yellow laminae, m. p. 181° , and, on treatment with alcoholic ammonia solution gives 3:5-dinitrophenylene-1:2-diamine (compare Nietzki and Hagenbach, Abstr., 1897, i, 277), m. p. 215° . (2) 2:4:6-Tribromo-3:5-dinitroaniline (compare Blanksma, *Rec. trav. chim.*, 1902, 21, 255).

T. H. P.

Preparation of *o*-Nitroamines from the Corresponding Phenol Derivatives. FRITZ ULLMANN and GÉZA NÁDAI (*Ber.*, 1908, 41, 1870—1878).—The authors find that when arylsulphonic esters of *m*-nitrophenol and its derivatives are treated with amines, they are converted into the corresponding *o*-nitroamines. Aniline acts only slowly on the ester of *o*-nitrophenol, but the reaction proceeds very quickly when the ester of 2:4-dinitrophenol is employed, thus:



It was not found possible to prepare the arylsulphonic ester of picric acid, and in presence of pyridine, quinoline, or diethylaniline, acetyl chloride was obtained. 2:4-Dinitrophenol, when treated with aluenesulphonyl chloride and diethylaniline, also gave a mixture of chlorodinitrobenzene and the sulphonic ester, but *o*- and *p*-nitrophenols

gave, under the same conditions, only the corresponding esters, whilst benzoic and cinnamic acids furnished the corresponding acid chlorides.

The 2:4-dinitrophenyl ester of *p*-toluenesulphonic acid crystallises from alcohol or glacial acetic acid in colourless prisms, m. p. 121°. When treated with gaseous ammonia in boiling nitrobenzene solution, it gives ammonium toluenesulphonate and 2:4-dinitroaniline, and, when warmed with aniline, 2:4-dinitrodiphenylamine is obtained. On reduction, the dinitro-ester gives the 2:4-diaminophenyl ester of *p*-toluenesulphonic acid, white leaflets, m. p. 125°; the diacetyl derivative, white needles, m. p. 167°. The dinitro-ester with pyridine gives dinitrophenylpyridinium toluenesulphonate, $C_{18}H_{15}O_7N_5S$, white needles.

When picric acid is heated with toluenesulphonyl chloride in presence of diethylaniline and nitrobenzene, and the product poured into ammonia, picramide is formed; when aniline is employed instead of ammonia, 2:4:6-trinitrodiphenylamine results, and with *p*-toluidine, 2:4:6-trinitrophenyl-*p*-tolylamine, red needles, m. p. 169°, is obtained. The 3:5-dinitrotolyl ester of *p*-toluenesulphonic acid, prepared from 3:5-dinitro-*p*-cresol and the acid chloride, feathery needles, m. p. 154°, when warmed with aniline in benzene solution gives phenyl-2:6-dinitro-*p*-tolylamine, orange leaflets, m. p. 174°.

Tri-*o*-cresol, when condensed with *p*-toluenesulphonyl chloride in presence of diethylaniline, yields 3-chloro-2:4:6-trinitrotoluene (Reverdin, Dresel, and Delétra, Abstr., 1904, i, 580). J. C. G.

A Violet *aci*-Ether of Hexanitrodiphenylamine. ARTHUR HANTZSCH and ST. OPOLOSKI (*Ber.*, 1908, 41, 1745—1749).—It has been found possible to isolate a *aci*-methyl ether of hexanitrodiphenylamine. The compound is deep violet in colour, and corresponds with the red *aci*-ethers of the nitrophenols.

The constitutional formula $C_6H_2(NO_2)_3 \cdot N : C_6H_2(NO_2)_3 \cdot NO \cdot OMe$ is suggested, whereas the ordinary yellow methyl ether is regarded as the *N*-ether, $C_6H_2(NO_2)_3 \cdot NMe \cdot C_6H_2(NO_2)_3$.

The silver derivative of hexanitrodiphenylamine is obtained most readily by the action of silver oxide on an acetone solution of the nitro-compound and subsequent precipitation with ether. It forms brilliant violet crystals, and decomposes above 200°. The salt reacts with a benzene solution of acetyl chloride, yielding the pale yellow *acetyl* derivative, $C_6H_2(NO_2)_3 \cdot NAc \cdot C_6H_2(NO_2)_3$, m. p. 240° (decomp.). The *N*-methyl and ethyl ethers are both yellow (compare Mulder, Abstr., 1906, i, 493), and give a red coloration with dilute alkalis only after hydrolysis. The ethers cannot be obtained by the action of picryl chloride or alkyl derivatives of picramide. A small amount of the violet *aci*-methyl ether (*O*-ether) is obtained when the dry silver salt is treated with excess of methyl iodide at 0° without the addition of a solvent. It crystallises from an absolutely dry mixture of benzene and hexane in black needles; it melts and decomposes at 140—141° when heated rapidly, or at 120° when heated slowly. Its solutions in benzene have a violet colour, and are comparatively stable.

The acetone solution is very unstable, and readily yields hexanitro-diphenylamine.

J. J. S.

Mutual Solubility of Solid Aromatic and the Corresponding Hexahydrogenated Compounds (Equilibrium in the System: Phenol-cyclohexanol.) LUIGI MASCARELLI and UGO PESTALOZZA (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 601—609. Compare Abstr., 1907, ii, 936).—The composition-freezing point diagram for mixtures of phenol and cyclohexanol consists of three branches: (1) from 0 to about 20% of cyclohexanol the freezing point falls continuously from 40° to about 19°; (2) from 20, to about 80—90% it rises slightly at first and afterwards falls rapidly to about -50°; (3) from 80—90 to 100% of cyclohexanol the freezing point rises from about -50° to +20°. In order to ascertain whether the slightly marked maximum of the second branch corresponds with the formation of an additive compound between the phenol and cyclohexanol, the equilibrium was studied in the presence of ethylurethane, which satisfies the conditions laid down by Mascarelli (compare this vol., ii, 94). As the maximum undergoes appreciable displacement towards the ordinate axis, it cannot correspond with an additive compound. On determining the composition of the separated crystals by Bylert's method (Abstr., 1891, 1411), using benzil as third substance, it is found that a solid solution is formed.

The results show that the two substances, phenol and cyclohexanol, are dimorphous, but only one form of the one compound can give solid solutions with one of the other. The ordinary forms of phenol and cyclohexanol are incapable of dissolving in the solid state, and should give a curve consisting of two straight lines, of which the first and third branches of the experimental curve form parts. The other forms of phenol and cyclohexanol are completely soluble in the solid condition, so that they should give a curve rising to a maximum; the second branch of the experimental curve represents part of this ideal curve. The existence of two forms of phenol is in accord with the observations of Tammann (*Krystallisieren und Schmelzen*, 1903, 308), who gave the m. p. of the unstable form of phenol as about 30°; the authors' results lead to the value 10—20°.

T. H. P.

Chlorinating Action of Phosphorus Pentachloride and the Action of Thionyl Chloride on Carbonyl Compounds. PAUL HOERING and F. BAUM (*Ber.*, 1908, 41, 1914—1918).—When boiled with a mixture of phosphorus tri- and penta-chlorides, isosafrole is converted into diisosafole (Angeli and Mola, Abstr., 1895, i, 24). Dibromo- and tribromo-isosafole, on the other hand, when heated with phosphorus pentachloride, form mixtures of stereoisomeric dichlorides, which are separated only partly and with difficulty. From dibromoisosafole there is obtained a dichloride, $C_{10}H_8O_2Cl_2Br_2$, m. p. 97—99°, and from the tribromo-compound a crystalline mixture, m. p. 134—145°, from which was isolated a dichloride, $C_{10}H_7O_2Cl_2Br_2$, m. p. 173.5—174.5°, or in one case 176—177°. This is stable towards water, but when heated gently with sodium ethoxide yields a crystalline product, m. p. 90—90.5°, containing only 1 atom of chlorine,

and when boiled with sodium acetate in glacial acetic acid solution is converted into an *acetate*, which, on hydrolysis with alcoholic potassium hydroxide, forms tribromoisosafrole oxide, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{Br}_3\cdot\text{CH} \begin{smallmatrix} \text{CHMe} \\ \diagup \\ \text{O} \end{smallmatrix}$;

hence the addition of chlorine must have taken place at the ethylene linking in the propenyl side-chain of the *isosafrole*. In agreement with this, it is found that the action of phosphorus pentabromide on di- and tri-bromoisosafrole leads to the formation of the dibromides, which are obtained also by direct addition of bromine.

Piperonal dichloride is formed by the action of thionyl chloride on piperonal, and, when heated with phosphorus pentachloride at $110\text{--}120^\circ$, yields dichloropiperonal dichloride, b. p. $163^\circ/18$ mm. (compare Barger, *Trans.*, 1908, 41, 1768). An attempt to found on this a general method of preparing dichlorides by the action of thionyl chloride on aldehydes was unsuccessful. Benzaldehyde, treated with thionyl chloride, yields benzyl chloride almost quantitatively; salicylaldehyde reacts with thionyl chloride or phosphorus pentachloride, forming disalicylide; anisaldehyde under similar conditions yields an unstable *product*, b. p. $125\text{--}130^\circ/14$ mm., which could not be purified; acetaldehyde and paraldehyde yield a mixture of products, b. p. $118\text{--}125^\circ$, whilst acetone reacts energetically with thionyl chloride, forming a *product* which decomposes on distillation and does not contain even traces of dichloropropane.

G. Y.

Derivatives of Diphenylene Oxide. WALTHER BORSCHKE and W. BOTHE (*Ber.*, 1908, 41, 1940—1944).—Although Galewsky (Abstr., 1891, 1234) was unable to obtain a mononitro-derivative of diphenylene oxide, the authors have prepared 4-nitrodiphenylene

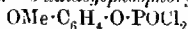
oxide, $\text{O} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \diagdown \quad \diagup \\ \text{C}_6\text{H}_3\cdot\text{NO}_2 \end{smallmatrix}$, by warming a glacial acetic acid solution of diphenylene oxide with nitric acid, D 1.52. It crystallises from acetic acid in yellow, silky needles, m. p. $181\text{--}182^\circ$. On reduction with tin and hydrochloric acid, it yields 4-aminodiphenylene oxide, m. p. 94° . The *hydrochloride*, decomp. 220° , the *stannichloride*, the *diacetyl* derivative, colourless needles, m. p. 83° , and the *benzoylamino*-derivative, m. p. 201° , are described. When the *diaz*-chloride is stirred into a solution of sodium sulphide and sodium hydroxide, sodium diphenylene-oxide-azosulphonate, $\text{C}_{12}\text{H}_7\text{O}\cdot\text{N}_2\cdot\text{SO}_3\text{Na}$, separates in yellow crystals. On acidification with acetic acid and treatment with zinc dust, sodium diphenylene-oxide-hydrazinesulphonate is formed, which on boiling with hydrochloric acid yields hydrazinodiphenylene oxide, $\text{C}_{12}\text{H}_{10}\text{ON}_2$, in leaflets, m. p. 152° . The *hydrochloride* has m. p. 225° . The chloride of diazodiphenylene oxide is not decomposed by boiling a solution with concentrated sulphuric acid; with phenol it forms phenolazodiphenylene oxide, reddish-brown crystals, m. p. 199° , which suffers the usual Sandmeyer decomposition, by means of which is obtained 4-iododiphenylene oxide, yellow leaflets, m. p. 182° , and the *nitride*, $\text{O} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \diagdown \quad \diagup \\ \text{C}_6\text{H}_3\cdot\text{CN} \end{smallmatrix}$, colourless needles, m. p. 120° , which on hydrolysis

furnishes *diphenylene-oxide-4-carboxylic acid*, colourless needles, m. p. 266°. This is also formed by treating acetyldiphenylene oxide (Galewsky, *loc. cit.*) with sodium hypochlorite. *Benzoyldiphenylene oxide*, $O\left\langle \begin{smallmatrix} C_6H_4 \\ C_6H_5Bz \end{smallmatrix} \right\rangle$, obtained from diphenylene oxide by treatment with benzoyl chloride and aluminium chloride, forms white needles, m. p. 167–168°, and gives an *oxime*, m. p. 234–235, the *benzoyl* derivative of which has m. p. 246°. J. C. C.

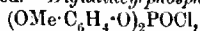
Hydrogenation of Polyphenols. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1908, 146, 1193–1196).—The authors have applied Sabatier and Senderens' method of hydrogenation by means of finely-divided nickel to quinol, catechol, and pyrogallol. At 160–170°, quinol yields a mixture of phenol, *cyclohexanol*, and *cis*- and *trans*-*cyclohexane-1:4*-diols. At 130°, the *cis*-compound is obtained exclusively. Catechol gives *cis-cyclohexane-1:2-diol*, rhombic crystals, m. p. 75–76°, b. p. about 225°. Pyrogallol is converted into *cyclohexane-1:2:3-triol*, tabular crystals, m. p. 67°. No definite product could be obtained from resorcinol, although a very small amount of a substance, m. p. 65°, was isolated, which was probably *cis-cyclohexane-1:3-diol*. J. C. C.

Melting Point of Resorcinol. CHARLES T. BENNETT (*Pharm. J.*, 1908, [iv], 26, 758).—After repeated crystallisation from benzene, resorcinol has m. p. 110°, although higher figures (up to 119°) are given in the literature. The sample was pure as estimated by Richard's method (titration with *N/5*-iodine), and contained neither catechol nor quinol. J. C. C.

Guaiacylphosphoric Acids. VICTOR AUGER and P. DUPUIS (*Compt. rend.*, 1908, 146, 1151–1153).—The authors have prepared mono- and diguaiacylphosphoric acids by the following three methods: (1) by boiling guaiacol with phosphoryl chloride, and hydrolysing the resulting guaiacylphosphoryl dichloride and diguaiacylphosphoryl chloride; (2) by treating a mixture of guaiacol and pyridine in the cold with phosphoryl chloride, and decomposing the pyridine salt with alkali (especially suitable for the preparation of diguaiacylphosphoric acid), and (3) by hydrolysing guaiacol phosphate with the calculated amount of alcoholic soda. *Guaiacylphosphoryl dichloride*,



is a colourless oil, b. p. 178–180°/30 mm., readily hydrolysed to *monoguaiacylphosphoric acid*, slender, deliquescent needles, m. p. 94°. The alkali salts are soluble in water, and the salts of the alkaline earths and of the heavy metals are insoluble; the sodium, calcium, and copper salts are described. *Diguiacylphosphoryl chloride*,

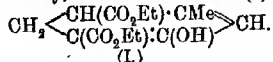


is a colourless oil, b. p. 258°/15 mm., slowly hydrolysed by water to *diguaiacylphosphoric acid*, colourless tablets, m. p. 97°. The sodium, calcium, and copper salts are described. The two latter are soluble in water, and may be used for the separation of mono- and diguaiacylphosphoric acids, as the corresponding salts of the mono-acid are

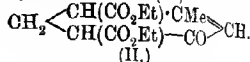
insoluble. The authors find that when guaiacol is heated with phosphoryl chloride and excess of pyridine, the methyl group is eliminated with formation of catechol.

J. C. C.

Tautomerism. IV. PAUL RABE (*Annalen*, 1908, 360, 289—298, Compare Abstr., 1906, i, 89).—The author finds that ethyl methylcyclohexenonedicarboxylate exists in two desmotropic modifications, namely, a solid enolic form (I) and an oily ketonic form (II):



(I)



(II)

Both modifications distil at the same temperature (200°/17 mm.), but do not yield an identical distillate; in each case about 20% of the one being converted into the other. This is the first proof of the existence of two desmotropic forms in a state of vapour.

[With DAVIN SPENCE and RICHARD EHRENSTEIN.]—1-Methyl-Δ¹-cyclohexen-3-one-4:6-dicarboxylate is obtained as an oil when ethyl 1-methylcyclohexan-1-ol-3-one-4:6-dicarboxylate is allowed to remain for two days in contact with hydrogen chloride in ethereal solution. After several days, crystals of the *enolic* form, m. p. 72°, separate, the residual oil consisting of the *ketonic* form. This has D_4^{20} 1.1687, n_D^{20} 1.4885; it is almost completely transformed into the enolic form by contact with piperidine or tripropylamine. Both modifications give a sodium salt, which, however, regenerates the enolic form. The same *p*-nitrophenylhydrazones, m. p. 165°, and semicarbazone, m. p. 162—164° (decomp.), were obtained from both the enolic and ketonic tautomers.

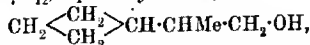
J. C. C.

The Action of Aluminium Chloride on Phenyl Mercaptan. J. J. B. DEUSS (*Rec. trav. Chim.*, 1908, 27, 145—148).—The addition of an excess of aluminium chloride to phenyl mercaptan, dissolved in large excess of light petroleum, results in the formation of diphenyl sulphide and diphenylene disulphide. Hydrogen sulphide is evolved together with a small quantity of hydrogen chloride.

W. O. W.

Transformations of cyclobutyl dimethylcarbinol. II. NICOLAI M. KJNER (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 676—698. Compare Abstr., 1905, i, 772).—The author has examined further the hydrocarbon C_7H_{12} , b. p. 100—102° (*loc. cit.*), and finds it to be identical with Rénard's heptene and with the hydrocarbon obtained by Maquenne from perseitol (Abstr., 1893, i, 635). The constitution of this hydrocarbon is probably $\text{CH}_2 \begin{array}{c} \text{CH}_2 \cdot \text{CMe} \\ | \\ \text{CH}_2 \cdot \text{CMe} \end{array}$.

The action of oxalic acid on cyclobutyl dimethylcarbinol yields, besides the hydrocarbon C_7H_{12} , a primary alcohol,



b. p. 157°/773 mm., m. p. 27—28°, D_4^{20} 0.9057, n_D^{20} 1.4489, molecular refraction 33.75 (calc. for cyclic alcohol, 33.74). Its phenylurethane, $\text{NHPh} \cdot \text{CO} \cdot \text{OC}_7\text{H}_{13}$, crystallises from light petroleum in long needles, m. p. 88—89°, and its acetate, $\text{C}_7\text{H}_{13} \cdot \text{OAc}$, has b. p. 171°/751 mm.

D_D^{25} 0.9403, n_D^{25} 1.4359. On oxidation with potassium dichromate and sulphuric acid, it yields an *aldehyde*, $C_6H_{11}CHO$, b. p. $144^\circ/751$ mm., D_D^{25} 0.9072, D_D^{20} 0.8985, n_D^{25} 1.4359, which forms a *semicarbazone*, $C_6H_{11}CH:N\cdot NH\cdot CO\cdot NH_2$, m. p. $188-189^\circ$, and an *oxime*, $C_6H_{11}CH:NOH$, m. p. 65° . The same aldehyde is obtained on oxidising *cyclobutyldimethylcarbinol*, the oxidation in this case being preceded by transformation into the primary alcohol described above.

The action of hydrobromic acid on this primary alcohol also yields a hydrocarbon, C_7H_{12} , identical with that obtained by the action of oxalic acid on *cyclobutyldimethylcarbinol*. The following are the physical characters of this hydrocarbon, which vary slightly with the source from which it is obtained, probably owing to admixture with the hydrocarbons $CH_2\begin{smallmatrix} CH_2 \\ CH_2 \end{smallmatrix}CH\cdot CMe\cdot CH_2$ and $CH_2\begin{smallmatrix} CH_2 \\ CH_2 \end{smallmatrix}C\cdot CMe_2$.

On treatment with concentrated sulphuric acid or hydriodic acid, the hydrocarbon C_7H_{12} is reduced to the compound C_7H_{14} (compare Maquenne, *loc. cit.*), b. p. $94-96^\circ/755-772$ mm., D_D^{20} 0.7546—0.7579, n_D^{20} 1.4144. Aschan (*Chemie der alicyclischen Verbindungen*, 473) regards this hydrocarbon C_7H_{14} as possibly identical with 1:3-dimethylcyclopentane, but the author regards it as, more probably, a mixture of 1:2-dimethylcyclopentane with a small proportion of methylcyclohexane.

The union of hydrogen bromide with the compound C_7H_{12} yields an unstable bromo-derivative, as also does the action of hydrobromic acid on the primary alcohol $C_7H_{13}\cdot OH$. The nitrosochloride, $C_7H_{12}\cdot NOCl$, prepared from the hydrocarbon C_7H_{12} , has m. p. $73-75^\circ$, and the dibromide, $C_7H_{12}Br_2$, m. p. $115-115.5^\circ$. The hexabromo-derivative, m. p. 134° , was also prepared (compare also Rénard, *Abstr.*, 1887, 565; Maquenne, *Abstr.*, 1889, 32, 361; 1892, 1065; Markownikoff, *Abstr.*, 1904, i, 384).

T. H. P.

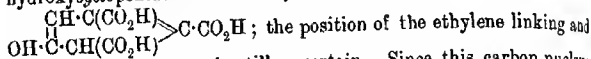
Cholesterol. STEFAN MINOVICI (*Ber.*, 1908, 41, 1561—1565).—A study of the action of sulphuric and hydrochloric acids on cholesterol (compare Mauthner, *Abstr.*, 1906, i, 579). Gradual addition of concentrated hydrochloric acid to cholesterol in boiling alcoholic solution leads to the formation of *cholesteryl ether*, $(C_{27}H_{43})_2O$ or $(C_{27}H_{45})_2O$, which crystallises in yellow needles, m. p. 74.5° , forms a viscid *additive* compound with bromine, gives a yellow, fluorescent coloration with concentrated hydrochloric acid, and is isomeric with Mauthner and Suida's ether (*Abstr.*, 1896, i, 425).

When heated on the water-bath with equal volumes of concentrated sulphuric acid and water, cholesterol yields (a) a *cholesteryl ether*, which forms white crystals, m. p. 201° , gives a yellow coloration, and fluorescence with concentrated sulphuric acid, and is considered to be isomeric with the preceding ether and Mauthner and Suida's ether; it forms a *tetrabromide*, $(C_{27}H_{43}Br_2)_2O$ or $(C_{27}H_{45}Br_2)_2O$, crystallising in needles, m. p. 174.5° (decomp.). (b) The *cholesteryl ether*, m. p. 74.5° ; and (c) a *substance*, which crystallises in spangles, m. p. $135-136^\circ$, and appears to form cholesterol on repeated recrystallisation.

G. Y.

Cholesterol, Cholic Acid, and a Common Degradation Product of the Same. HUGO SCHRÖTTER, RICHARD WEITZENBÖCK, and REINHOLD WITT (*Monatsh.*, 1908, 29, 245—254).—Both cholesterol and cholic acid, when heated with concentrated sulphuric acid in the presence of a small quantity of mercury, yield a mixture of acids, which when treated with strong nitric acid yields *rhizocholic acid*, $C_{26}H_{46}O_7$, crystallising in small, white needles, m. p. 228—230°; the silver salt, $C_{26}H_{46}O_7Ag_3$, is a white precipitate; the barium and calcium salts are more soluble in cold than in hot water.

Since the acid is so stable towards concentrated sulphuric acid and nitric acid, the three carboxylic groups are evidently attached to three different carbon atoms. It is therefore suggested that the acid is a hydroxycyclopentanedicarboxylic acid having the composition



the position of the ethylene linking and of the hydroxyl group is still uncertain. Since this carbon nucleus is characteristic of terpenes and camphenes, it is concluded that not only do cholesterol and cholic acid have a similar structure, but are also connected with the terpenes.

W. H. G.

Non-hydrolysable Constituents of Cacao Butter. HERMANN MATTHÉ and O. KÖHNIG (*Rev.*, 1908, 41, 1591—1592).—The two phytosterols, obtained previously from cacao butter (*this vol.*, p. 139), are best prepared from crude phytosterol acetate; this is brominated in glacial acetic acid solution, and the bromides separated, reduced, and hydrolysed. Phytosterol acetate tetrabromide yields phytosterol, which crystallises in monoclinic leaflets, m. p. 162—163° (stigmasterol, m. p. 146°: *loc. cit.*). Phytosterol acetate dibromide yields phytosterol, which forms doubly refracting, hexagonal crystals, m. p. 133° (135—136°: *loc. cit.*).

Phytosterol and a yellow, unsaturated oil with a pleasant odour are obtained on hydrolysis of the fat extracted from cacao shells by light petroleum.

G. Y.

Hydrogenation of cyclobutanecarboxylic Acid. NICOLA M. KJNER (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 673—676).—In order to throw light on the formation of a 5-carbon atom ring compound from cyclobutyl dimethylcarbinol by the action of hydriodic acid (compare Abstr., 1905, i, 772), the author has investigated the action of hydriodic acid (D 1.96) on cyclobutanecarboxylic acid. When these compounds are heated together in a sealed tube at 200—210° for nine hours, the products obtained are: (1) a small quantity of a substance, b. p. about 150°, having a hydrocarbon-like odour; (2) *n*-valeric acid, which represents the main product. The hydrogenation of cyclobutanecarboxylic acid thus differs from that of cyclobutyl dimethylcarbinol in that it leads merely to the breaking of the tetramethylene ring at a position adjacent to the carboxyl group with formation of an open-chain compound.

T. H. P.

The Six Dinitrobenzoic Acids. H. A. STRECK (*Rec. trav. Chim.*, 1908, 27, 207—250).—This paper consists chiefly of work already published (compare Abstr., 1907, i, 131). Full details are given of

the preparation of the dinitrotoluenes and the corresponding dinitrobenzoic acids. Determinations of the constants of dissociation and esterification disclose the fact that these acids may be divided into two classes. The first includes the two acids in which a nitro-group does not adjoin the carboxyl group; these are only slightly dissociated in solution, and show a comparatively high value for the esterification constant. The four remaining acids, however, are much more highly dissociated, and exhibit correspondingly small values for the esterification constant.

A description and sketch is given of an apparatus suitable for the extraction of large quantities of liquid by means of ether.

W. O. W.

Chloromethyl Sulphate. II. Action on Amino-groups.
JOSEF HOUBEN and HANS R. ARNOLD (*Ber.*, 1908, 41, 1565—1580, Compare Abstr., 1907, i, 1000).—The action of water on chloromethyl sulphate, $\text{CH}_2\text{Cl}\cdot\text{SO}_4\text{Me}$, was found previously to lead to the formation of methylsulphuric acid, formaldehyde, and hydrogen chloride; from this it appears that the chloromethyl is more reactive than the methyl group. Hence it was to be expected that the employment of chloromethyl sulphate as a methylating agent would lead to the formation of chloromethyl derivatives. This has been realised in the case of the three aminobenzoic acids. Anthranilic acid and chloromethyl sulphate form the methosulphate of chloromethylanthranilic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\text{Cl}\cdot\text{HMeSO}_4$, which readily loses hydrogen chloride, forming the methosulphate of methyleneanthranilic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{CH}_2\cdot\text{HMeSO}_4$ (Mehner, Abstr., 1901, i, 470; 1902, i, 676). The methyleneanthranilic acid, when liberated, rapidly polymerises, hence the yield of cyanomethylanthranilic acid formed from it by the action of potassium cyanide and hydrogen chloride is the less the longer the methylene acid has been in the free state. *m*- and *p*-Aminobenzoic acids behave in the same manner as the *o*-amino-acid.

The action of chloromethyl sulphate on methylantranilic acid leads to the formation of a substance, which is probably *methylenebis-methyldiantranilic acid*, $\text{CH}_2(\text{NMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H})_2$, and must be formed by loss of hydrogen chloride from a mol. of methyl chloromethylanthranilic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}\cdot\text{CH}_2\text{Cl}$, and a mol. of unchanged methylantranilic acid, $\text{NHMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$.

The action of chloromethyl sulphate on ammonia and substituted ammonias has also been studied. Whilst the action of chloromethyl sulphate on ammonia leads to the formation of methylamine hydrochloride, hexamethylenetetramine, and ammonium sulphate, diethylamine yields tetraethylmethylenediamine or, under special conditions, chloromethyldiethylamine. Primary and secondary aromatic amines react similarly, forming derivatives of methylenediamine.

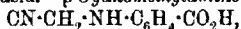
The following substances are new:

Methyleneanthranilic acid, $(\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{CH}_2)_n$, is obtained as a golden-yellow powder, which darkens at 190° , m. p. 210° , is soluble in acids or alkalis, and yields a green copper, white ferrous, and dark

brown ferric salt. When treated with concentrated alcoholic hydrogen chloride, the acid yields an unstable product, which may be its hydrochloride or chloromethylantranilic acid.

Chloromethyl sulphate and methyl anthranilate yield a substance, which is probably the methyl ester of the polymeric methylene-anthranilic acid, and on reduction with zinc and hydrochloric acid forms polymeric methyleneanthranilic acid together with traces of methylantranilic acid.

p-Methyleneaminobenzoic acid, $(C_8H_7O_2N)_n$, is obtained as a white precipitate, darkening at 220° , decomp. 250° , and absorbs hydrogen chloride, forming a brown, deliquescent acid, which may be *p*-chloro-methylaminobenzoic acid. *p*-Cyanomethylaminobenzoic acid,

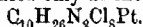


prepared together with a small amount of a substance, crystallising in white needles, m. p. 225° , from *p*-aminobenzoic acid, formaldehyde, and hydrogen cyanide, or in small amounts by adding potassium cyanide to *p*-methyleneaminobenzoic acid dissolved in dilute hydrochloric acid, forms a white, crystalline powder, m. p. 177° (decomp.).

m-Methyleneaminobenzoic acid, $(C_8H_7O_2N)_n$, is obtained as a yellowish-brown powder, decomp. 260° , which absorbs hydrogen chloride, forming an unstable, reddish-brown product.

m-Cyanomethylaminobenzoic acid, $C_8H_7O_2N_2$, prepared from *m*-aminobenzoic acid, crystallises in yellowish-brown leaflets, m. p. 193° . The product, obtained in small amount by the action of potassium cyanide and hydrochloric acid on *m*-methyleneaminobenzoic acid, has m. p. 182° .

Chloromethyldiethylamine, $NEt_2 \cdot CH_2Cl$, prepared by the action of chloromethyl sulphate on diethylamine at low temperatures, is unstable and can be isolated only as the platinumchloride,



Tetraphenylmethylenediamine, $C_{25}H_{22}N_2$, prepared from chloromethyl sulphate and diphenylamine, forms an unstable, white, crystalline mass, m. p. $82-85^\circ$, is soluble in concentrated acids, and gives with nitrous acid a green oil dissolving to a bluish-green solution in ether.

s-Diphenyldiethylmethylenediamine, $CH_2(NPhEt)_2$, prepared from ethylaniline, crystallises from acetone in leaflets, m. p. 145° .

Di-p-bromo-s-diphenylmethylenediamine, $CH_2(NH \cdot C_6H_4Br)_2$, from *p*-bromo aniline, crystallises in white leaflets, m. p. 181° (decomp.); the sulphate, $C_{18}H_{14}N_2Br_2SO_4$, rhombic plates.

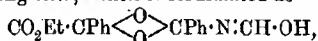
The *di-m-bromo* compound forms leaflets, m. p. 135° . 2:2'-Dinitro-*s-di-p-tolylmethylenediamine* $CH_2(NH \cdot C_6H_3Me \cdot NO_2)_2$, from 2-nitro-*p*-toluidine, crystallises in brown needles, m. p. 207° ; the sulphate forms yellowish-white needles. These derivatives of methylenediamine, when heated with sulphuric acid, yield formaldehyde and the corresponding amines.

G. Y.

Separation of Hippuric Acid from Urine. HERBERT E. ROAF (*Bio. Chem. J.*, 1908, 3, 185-187).—To each litre of herbivorous urine, 250 grams of ammonium sulphate and 15 c.c. of concentrated sulphuric acid are added. The hippuric acid then crystallises out readily, and with a comparatively small amount of adherent urinary

pigment. This can be removed by recrystallisation after boiling with animal charcoal. W. D. H.

Bisbenzoyl Cyanide. OTTO DIRLS and ALBERT FILLOW (*Ber.*, 1908, 41, 1893—1901).—A substance having the composition of benzoyl cyanide, but not identical with it or with trisbenzoyl cyanide, which was obtained by Wache (*Abstr.*, 1889, 684) by the action of sodium on benzoyl cyanide, and by Claisen (*Abstr.*, 1898, i, 423) by treating benzoyl chloride with hydrogen cyanide in presence of pyridine, is now found to be hisbenzoyl cyanide. It is considered to have the constitution $\text{CN}\cdot\text{CPh}\langle\text{O}\rangle\text{CPh}\cdot\text{NC}$, because (1) it does not give ketone reactions. (2) When treated with alcoholic hydrogen chloride, it forms an additive compound with 1 mol. of water, whilst at the same time one cyanogen group is converted into a carbethoxy-group; the resulting ester, which is formulated as



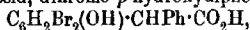
crystallises in prisms, m. p. 143—144°, forms with phenylcarbimide an additive compound, $\text{C}_{25}\text{H}_{22}\text{O}_6\text{N}_2$, crystallising in short prisms, m. p. 163—164°, and when treated with alkalis is hydrolysed, yielding benzoylformic acid, benzamide, formic acid, and ethyl alcohol. (3) Treatment of bisbenzoyl cyanide with hydriodic acid leads to the formation of an amide, $\text{NH}_2\cdot\text{CO}\cdot\text{CPh}\langle\text{O}\rangle\text{CPh}\cdot\text{NC}$, which crystallises in rhombic prisms, m. p. 174—177° (decomp.), cannot be converted into the preceding ester by treatment with alcoholic hydrogen chloride, and is hydrolysed by alkalis, yielding benzoylformamide, benzoic acid, and hydrogen cyanide; and (4) bisbenzoyl cyanide forms an amidoxime, $\text{OH}\cdot\text{N}\cdot\text{C}(\text{NH}_2)\cdot\text{CPh}\langle\text{O}\rangle\text{CPh}\cdot\text{NC}$, which crystallises in rectangular prisms, m. p. 181° (decomp.), and on hydrolysis yields benzoic acid, hydrogen cyanide, and benzoylformamidoxime, $\text{COPh}\cdot\text{C}(\text{NH}_2)\cdot\text{N}\cdot\text{OH}$, crystallising in quadratic prisms, m. p. 133—134°. When treated successively with phosphorus pentachloride in ethereal solution and with ice, this undergoes Beckmann's transformation, yielding benzoyl-carbamide. G. Y.

Synthesis of Polypeptides. EMIL ABDERHALDEN and MARKUS GUGGENHEIM (*Ber.*, 1908, 41, 1991).—In the paper XV on the derivatives of 2:5-di-iodo-*L*-tyrosine (this vol., i, 420), the figures should be 3:5 in place of 2:5 throughout. C. S.

Liberation of Carbon Monoxide from Secondary and Primary Carboxylic Acids. AUGUSTIN BISTRZYCKI and B. VON SIEMIRADZKI (*Ber.*, 1908, 41, 1665—1672. Compare Oechsler de Couineck and Raynaud, *Abstr.*, 1903, i, 457, 458).—In continuation of the work previously published (*Abstr.*, 1906, i, 135), the liberation of carbon monoxide from various secondary and primary carboxylic acids when heated with concentrated sulphuric acid has been investigated. Most of the secondary acids studied, when heated with sulphuric acid, evolve roughly two-thirds to three-quarters of the theoretical amount

of carbon monoxide, whilst the primary acids yield relatively far less carbon monoxide. As a rule, the stability of the normal primary acids decreases with an increase in the number of methylene groups, whilst the normal acids are more stable than their isomerides with side-chains.

The secondary acids investigated were diphenylacetic acid, tetra-nitrodiphenylacetic acid, dihydro-*p*-hydroxydiphenylacetic acid,

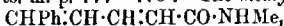


2:5-dimethylhydratropic acid, $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, hexahydrobenzoic acid, quinic acid, and sulphocamphyllic acid. The last acid is very stable towards sulphuric acid; when camphoric acid is heated with sulphuric acid at 200°, only slightly more than 1 mol. of carbon monoxide is evolved from 1 mol. of the acid, showing that the introduction of a sulphonic group into the acid radicle prevents the evolution of carbon monoxide. The primary acids studied were butyric acid, isobutyric acid, α -ethylbutyric acid, valeric acid, isovaleric acid, hexoic acid, and γ -methylvaleric acid.

W. H. G.

Action of Ammonia and Amines on Cinnamylacrylic [Cinnamylideneacetic] Acid and its Methyl Ester. ADOLF RIEDL (*Annalen*, 1908, 361, 96—108).—Hinrichsen observed (Abstr., 1904, i, 1012) that cinnamylideneacetic acid and its salts do not react with phosphorus pentachloride. This is in agreement with Meyer's observation (Abstr., 1901, i, 407) that acids with conjugated double linkings, if containing a second negative group in the δ -position to the carboxyl, are, in general, incapable of forming acid chlorides. The present author has found that methyl cinnamylideneacetate does not react with phosphorus pentachloride, but has obtained the amide in about an 8% yield by heating the methyl ester with alcoholic ammonia at 140—160°. Primary aliphatic amines, and to a very small extent secondary amines, such as diethylamine and piperidine, react with methyl cinnamylideneacetate in the same manner as does ammonia. Primary aromatic amines, on the other hand, do not react with the ester when boiled in a reflux apparatus, whilst at higher temperatures complete decomposition takes place. When heated with cinnamylideneacetic acid, aniline and *o*-toluidine form salts.

Cinnamylideneacetamide, $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}_2$, crystallises in yellow leaflets, m. p. 185°, decolorises bromine and permanganate solutions, and when heated with acetic anhydride in benzene solution yields the *acetyl* derivative, $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{NHAc}$, crystallising in yellow leaflets, m. p. 177—178°. The *methylamide*,



crystallises in white needles, m. p. 157°; the *ethylamide*, $\text{C}_{13}\text{H}_{15}\text{ON}$, white needles, m. p. 143—144°; the *propylamide*, $\text{C}_{14}\text{H}_{17}\text{ON}$, white needles, m. p. 133°; the *butylamide*, $\text{C}_{15}\text{H}_{19}\text{ON}$, white crystals, m. p. 119—120°; the *diethylamide*, $\text{C}_{16}\text{H}_{21}\text{ON}$, white crystals, m. p. 106°; the *piperidide*, $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{NC}_5\text{H}_{10}$, colourless leaflets, m. p. 203° (decomp.).

The cinnamylideneacetates of the following bases are described, the temperatures are melting points. Methylamine, white needles, 142—143°; ethylamine, white leaflets, 117—118°; propylamine,

white leaflets, 140° (decomp.); butylamine, white leaflets, 107—108°; aniline, greenish-white needles, 184°; *o*-toluidine, reddish-white needles; diethylamine, crystalline varnish, 80°; piperidine, white prisms, 111°; guanidine, yellowish-white leaflets, 220°. G. Y.

3:5-Dinitro-4-hydroxybenzoic Acid. FRÉDÉRIC REVERDIN (*Bull. Soc. chim.*, 1908, [iv], 3, 591—593; *Arch. sci. phys. nat.*, 1908, 25, 474—478).—This acid, first prepared by Barth (*Zeit. Chem.*, 1866, 647) by nitration of *p*-hydroxybenzoic acid, was subsequently obtained by Salkowski from chrysanic acid (*Abstr.*, 1872, 555), but the latter investigator expressed doubt as to the identity of the two acids. The results of the present work, undertaken to decide this point, show that the two are identical.

p-Hydroxybenzoic acid, nitrated by Barth's method, yields in addition to 3:5-dinitro-4-hydroxybenzoic acid, 3-nitro-4-hydroxybenzoic acid and 2:4-dinitrophenol. The ethyl ester of the dinitro-acid can be obtained by direct nitration of ethyl *p*-hydroxybenzoate. The methyl ester, m. p. 115—116°, similarly obtained, crystallises in colourless, prismatic needles, and is readily hydrolysed by ebullition with sodium carbonate solution. The dinitro-acid itself is best obtained by nitrating *p*-hydroxybenzoic acid dissolved in sulphuric acid and kept at 0°, with a mixture of equal parts of sulphuric acid and nitric acid (D 1.52). 3:5-Diamino-4-hydroxybenzoic acid, m. p. 205°, obtained by reducing the dinitro-acid with tin and hydrochloric acid, is readily oxidisable. The hydrochloride and sulphate are crystalline. T. A. H.

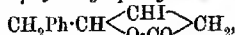
Action of Nascent Hypoiodous Acid on Unsaturated Acids. Iodo-lactones. J. BOUGAULT (*Ann. Chim. Phys.*, 1908, [viii], 14, 145—183).—The first part of the paper contains an epitome of previous work (compare *Abstr.*, 1905, i, 9; 1906, i, 848; 1908, i, 179, 269). A number of new iodo-lactones are described; these have been obtained by the action of mercuric oxide and iodine on $\beta\gamma$ - or $\gamma\delta$ -unsaturated acids.

$\alpha\alpha$ -Dimethyl- Δ^2 -pentenoic acid yields the lactone of β -iodo- γ -hydroxy- $\alpha\alpha$ -dimethylvaleric acid, $\text{CHI} \begin{array}{c} \text{CMe}_2 \cdot \text{CO} \\ \text{CHMe} \end{array} \text{O}$, m. p. 86°, a colourless, crystalline, neutral substance having a camphoraceous odour. $\alpha\alpha$ -Dimethylisocrotonic acid forms the lactone of β -iodo- γ -hydroxy- $\alpha\alpha$ -dimethylbutyric acid, $\text{CHI} \begin{array}{c} \text{CMe}_2 \\ \text{CH}_2 \cdot \text{O} \end{array} \text{CO}$, a yellow liquid, which, like the preceding lactone, has a camphoraceous odour and is decomposed on boiling with aqueous sodium hydroxide.

The lactone of β -iodo- γ -hydroxyhexoic acid, $\text{CHI} \begin{array}{c} \text{CH}_2 \cdot \text{CO} \\ \text{CHEt} \end{array} \text{O}$, prepared from Δ^2 -hydrosorbic acid, is a thick, yellow liquid, decomposing when distilled under atmospheric pressure. Fittig's α -hydroypiperic acid furnishes the lactone of β -iodo- γ -hydroxy- δ -3:4-methylenedioxy-phenylvaleric acid, $\text{CH}_2\text{O}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CH}_2 \cdot \text{CH} \begin{array}{c} \text{CHI} \cdot \text{CH}_2 \\ \text{O} - \text{CO} \end{array}$, yellow crystals, m. p. 104°. Aqueous sodium hydroxide converts this into

the γ -ketonic acid, $\text{CH}_3\text{O}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, whilst ammonium sulphite transforms it into the ammonium salt of a new sulphonic acid, $\text{CH}_3\text{O}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}\left\langle\begin{smallmatrix}\text{CH}(\text{SO}_2\text{NH}_4)\\\text{O}-\text{CO}\end{smallmatrix}\right\rangle\text{CH}_2$, which crystallises from hot water in glistening plates. The corresponding barium salt crystallises with $2\text{H}_2\text{O}$, and, when oxidised by potassium permanganate, furnishes piperonylic acid, homopiperonylic acid, and methylenedioxyphenylglyoxylic acid.

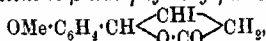
The lactone of β -iodo- γ -hydroxy- δ -phenylvaleric acid,



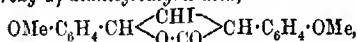
forms yellow crystals, m. p. 83° , and is prepared from hydrocinnamylideneacetic acid. Sodium hydroxide transforms it into the corresponding γ -ketonic acid, and in its behaviour with ammonium sulphite it resembles the preceding lactone. The barium salt has the composition $(\text{C}_{11}\text{H}_{11}\text{O}_2\text{SO}_3)_2\text{Ba}\cdot 3\text{H}_2\text{O}$. Phenylisocrotonic acid is the starting point for the preparation of the lactone of β -iodo- γ -hydroxy- γ -phenyl-

butyric acid, $\text{CHPh}\left\langle\begin{smallmatrix}\text{CHI}\\\text{O}-\text{CO}\end{smallmatrix}\right\rangle\text{CH}_2$, m. p. 116° . This compound differs from the two foregoing lactones in its behaviour towards sodium hydroxide and ammonium sulphite. The lactone of β -iodo- γ -hydroxy-

α,δ -diphenylvaleric acid, $\text{CH}_2\text{Ph}\cdot\text{CH}\left\langle\begin{smallmatrix}\text{CHI}\\\text{O}-\text{CO}\end{smallmatrix}\right\rangle\text{CHPh}$, yellow crystals, m. p. 106° , is obtained from Rebuffat's hydrophenylcinnamylideneacetic acid. The lactone of β -iodo- γ -hydroxy- γ -anisylvaleric acid,

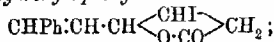


m. p. 125° , is prepared from anisylisocrotonic acid. The lactone of β -iodo- γ -hydroxy- α,γ -dianisylbutyric acid,



yellow crystals, m. p. 115° , is obtained from Fittig's dianisylpentenoic acid.

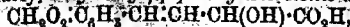
The two following iodo-lactones are obtained from unsaturated acids of the general formula $\text{CHR}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$. The lactone of γ -iodo- δ -hydroxyvaleric acid, $\text{CHI}\left\langle\begin{smallmatrix}\text{CH}_2\cdot\text{CH}_2\\\text{CH}_2-\text{O}\end{smallmatrix}\right\rangle\text{CO}$, is a liquid, becoming brown on exposure and decomposing when distilled. The lactone of γ -iodo- δ -hydroxy- δ -phenylvaleric acid, $\text{CHI}\left\langle\begin{smallmatrix}\text{CH}_2\cdot\text{CH}_2\\\text{CHPh}\cdot\text{O}\end{smallmatrix}\right\rangle\text{CO}$, forms yellow crystals, m. p. 90° . Cinnamenylisocrotonic acid yields the lactone of β -iodo- γ -hydroxy- ϵ -phenyl- Δ^6 -hexenoic acid,



this is sparingly soluble in alcohol and has m. p. 125° .

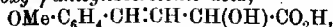
Anisylpyruvic acid, on partial reduction with sodium amalgam, gives α -hydroxy- γ -phenylisocrotonic acid, $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$. This was not isolated, but on treating an aqueous solution of its sodium salt with iodine the lactone of β -iodo- α,γ -dihydroxy- γ -phenylbutyric acid, $\text{CHI}\left\langle\begin{smallmatrix}\text{CH}(\text{OH})\\\text{CHPh}\cdot\text{O}\end{smallmatrix}\right\rangle\text{CO}$, was formed. This occurs as yellow crystals, which darken at 125° and melt with decomposition at 132° . It

is much more soluble in the ordinary media than the preceding lactones. Similarly, α -hydroxy- γ -piperonylisocrotonic acid,

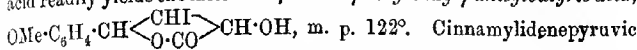


m. p. 143° , furnishes the lactone of β -iodo- $\alpha\gamma$ -dihydroxy- γ -methylenedioxy-butyric acid, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}\begin{smallmatrix} \text{CHI} \\ \text{O}\cdot\text{CO} \end{smallmatrix}\text{CH}\cdot\text{OH}$, small, yellow needles,

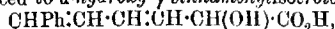
m. p. 150° . When anisylidenepyruvic acid is partly reduced by sodium amalgam, α -hydroxy- γ -anisylisocrotonic acid,



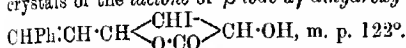
m. p. 145° , is obtained together with α -hydroxy- γ -anisylbutyric acid, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$, m. p. 116 – 117° . The former acid readily yields the lactone of β -iodo- $\alpha\gamma$ -dihydroxy- γ -anisylbutyric acid,



Cinnamylidenepyruvic acid can be reduced to α -hydroxy- γ -cinnamylisocrotonic acid,

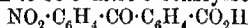


the sodium salt of which reacts readily with iodine to form yellow crystals of the lactone of β -iodo- $\alpha\gamma$ -dihydroxy- ϵ -phenyl- Δ^5 -hexenoic acid,



The following $\beta\gamma$ -unsaturated acids having a ketonic group in the α -position cannot be made to yield iodo-lactones: piperonylidene-pyruvic acid, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{CO}_2\text{H}$, m. p. 161° ; anisylidenepyruvic acid, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{CO}_2\text{H}$, m. p. 131° ; furfurylidene-pyruvic acid, $\text{C}_4\text{H}_4\text{O}\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{CO}_2\text{H}$, m. p. 111° ; p-methoxyhydratropylidenepyruvic acid, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHMe}\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{CO}_2\text{H}$, m. p. 180° .
W. O. W.

Nitrobenzoylbenzoic Acids. J. RAINER (*Monatsh.*, 1908, 29, 177–180).—The compound obtained by Lang (*Abstr.*, 1905, i, 895) by adding *o*-benzoylbenzoic acid to nitric acid (1:52), and described as being identical with Kliegl's *p*-nitro-*o*-benzoylbenzoic acid (*Abstr.*, 1905, i, 187), is shown to be 3'-nitro-*o*-benzoylbenzoic acid,



(compare Basler Chemische Fabrik, *Abstr.*, 1904, i, 512). A compound was obtained in the preparation of *p*-nitro-*o*-benzoylbenzoic acid by Kliegl's method which is probably *m*-nitro-*o*-benzoylbenzoic acid, $\text{COPh}\cdot\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{CO}_2\text{H}$; it crystallises in rectangular leaflets, m. p. 212° .
W. H. G.

Reactions of Dicarboxylic Anhydrides with Magnesium Organic Compounds. JOSEF HOUBEN and ARNOLD HAHN (*Ber.*, 1908, 41, 1580–1588).—The authors have studied the action of magnesium organic compounds on camphoric anhydride. As this reaction takes place less simply (Komppa, this vol., i, 352) than that with the anhydrides of monocarboxylic acids or with phthalic anhydride, the study has been extended to other dicarboxylic anhydrides. It is found that, whilst phthalic, naphthalic, camphoric, and citraconic anhydrides react readily, the last with almost explosive violence, with magnesium organic compounds, succinic anhydride reacts with great difficulty, and to an almost complete extent only in boiling toluene solution. With succinic anhydride, the reaction leads to the formation of products, $\text{C}_2\text{H}_4(\text{CR}_2\cdot\text{OH})_2$ in which the two

carbonyl oxygen atoms are displaced each by two alkyl groups. Thus succinic anhydride and magnesium phenyl bromide yield tetraphenylbutandiol, m. p. 205—206° (Dilthey and Last, Abstr., 1904, i, 667). Camphoric anhydride, on the other hand, forms isomeric campholides (annexed formulae), two alkyl groups being substituted for only one of the two carbonyl oxygen atoms.

aaδδ-Tetrabenzylbutan-αδ-diol, $\text{OH}\cdot\text{C}(\text{C}_7\text{H}_7)_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}(\text{C}_7\text{H}_7)_2\cdot\text{OH}$, prepared from succinic anhydride and magnesium benzyl chloride, crystallises in needles, m. p. 129°, and gives a red coloration with concentrated sulphuric acid. The by-products of the reaction are probably unsaturated hydrocarbons or benzylated hydrofurans.

The action of magnesium ethyl bromide on succinic anhydride leads to the formation of *tetraethylhydrofuran*, $\text{C}_{12}\text{H}_{24}\text{O}$, which is obtained as an oil, b. p. about 80—120°/11 mm.

Camphoric anhydride and magnesium benzyl chloride form two dibenzylcampholides, $\text{C}_8\text{H}_{14}\left\langle\begin{array}{c} \text{C}(\text{C}_7\text{H}_7)_2 \\ \text{CO} \end{array}\right\rangle\text{O}$, which are separated by means of the sodium salts of the corresponding hydroxycampholic acids.

a-Dibenzylhydroxycampholic acid, $\text{CO}_2\text{H}\cdot\text{C}_8\text{H}_{14}\cdot\text{C}(\text{C}_7\text{H}_7)_2\cdot\text{OH}$, crystallises in needles containing alcohol of crystallisation, m. p. 177—178°, and is electrified when dried and rubbed. The sodium salt is sparingly soluble; the barium salt was analysed. *a-Dibenzylcampholide* is best prepared by boiling the acid with acetyl chloride, or by distillation of the acid in a vacuum; it forms prisms, m. p. 118°.

b-Dibenzylhydroxycampholic acid crystallises in needles, m. p. 145°. *b-Dibenzylcampholide* crystallises in needles, m. p. 114°. A mixture of the two dibenzylcampholides has m. p. about 50°. The allocation of the two constitutions requires further investigation. G. Y.

Preparation of Benzoic Acid. HANS VON LIEBIG (*Ber.*, 1908, 41, 1644—1645).—A 90—95% yield of this acid, free from benzoic acid, and therefore much better than that ordinarily obtained, results when 100 grams of benzil are boiled with a 50% aqueous solution of 100 grams of potassium hydroxide and 200 grams of alcohol for ten to twelve minutes; the mass is then left for several hours before collecting the salt, which is well washed with alcohol, then dissolved in cold water, heated to boiling, and the benzoic acid precipitated with sulphuric acid. W. R.

Tritanocarboxylic Acids. HANS VON LIEBIG (*Ber.*, 1908, 41, 1645—1648. Compare Abstr., 1905, i, 781; 1907, i, 45, 930—1045; this vol., i, 445).—Cooled sulphuric acid gives in the condensation of benzil with hydroxybenzenes fairly good yields of *p*-hydroxytritanic acids, but poor yields of the ortho-acids. In order to obtain these acids in better yields, benzoic acid has been substituted, and experiments carried out by heating the molten acid with the phenol, the fusion treated twice with boiling water and then twice with 5% sodium carbonate to remove the free hydroxytritanic acid; the residue consists of lactone.

Resorcinol gives an almost quantitative yield of 2:4-dihydroxytritanolactone (1905, *loc. cit.*), and phenol an 80–90% yield of *p*-hydroxytritanic acid (Bistrzycki and Nowakowski, Abstr., 1901, i, 716) and 10–20% of *o*-hydroxytritanolactone (1907, *loc. cit.*).

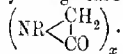
o-Cresol leads to the formation of 2-hydroxy-3-methyltritanolactone, $C_{21}H_{18}O_5$, which crystallises from alcohol in stout needles, m. p. 136–137°, and 4-phenoxy-3-methyltritanic acid, which sinters at 130°, froths at 140–143°, and is thereby converted into the anhydride, $C_{16}H_{14}O_5$, m. p. 215°. *m*-Cresol gives 4-hydroxy-2-methyltritanic acid and 2-hydroxy-4-methyltritanolactone (Bistrzycki and Nowakowski, *loc. cit.*). *p*-Cresol, in addition to the lactone (m. p. 132°: Bistrzycki gives 130°) and the *p*-acid, gives the 5:5'-ether of 4:4'-dihydroxy-2:2'-dimethyltritanic acid, $C_{42}H_{34}O_5$, which crystallises from benzene in needles, m. p. 245°.

Thymol yields the *p*-hydroxy-acid (Geipert, Abstr., 1904, i, 319) and a small quantity of 2-hydroxy-3-methyl-6-isopropyltritanolactone, crystallising in leaflets, m. p. 124°. Quinol gives 2:5-dihydroxytritanolactone (m. p. 200–201°: Tarczynsky, Diss., Freiburg, gives 194°). Methyl 2:5-dimethoxytritanate, $C_{23}H_{22}O_6$, crystallises in glistening leaflets from alcohol, m. p. 133°. Catechol gives 2:3-dihydroxytritanolactone, which separates from alcohol in fine crystals, m. p. 136°.

Guaiacol gives a mixture, one constituent of which is probably 4-hydroxy-3-methoxytritanic acid, $C_{21}H_{18}O_6$, crystals, m. p. 194°. Orcinol leads to the formation of 2:4-dihydroxy-6-methyltritanolactone, $C_{21}H_{18}O_5$, the crystals of which contain benzene of crystallisation, m. p. 177°, after warming, and pyrogallol yields 2:3:4-trihydroxytritanolactone, $C_{20}H_{14}O_5$, large crystals from benzene, m. p. 184°.

W. R.

Anhydrides of α -Amino-*N*-carboxylic Acids and of α -Amino-acids. HERMANN LEUCHS and WALTER GEIGER (*Ber.*, 1908, 41, 1721–1726. Compare Abstr., 1906, i, 236; 1907, i, 770).—Anhydrides have been obtained by the action of thionyl chloride on the carbomethoxy-derivatives of *C*-phenylaminoacetic acid, phenylalanine, and leucine. The anhydrides crystallise well, and have low melting points. They are readily decomposed by water or absolute alcohol, yielding carbon dioxide and amorphous compounds of the type



N-Carbomethoxy *C*-phenylglycine, $\text{CO}_2\text{Me} \cdot \text{NH} \cdot \text{CHPh} \cdot \text{CO}_2\text{H}$, crystallises from water or benzene in needles, m. p. 87–88°. The anhydride, $\text{CHPh} \begin{array}{c} \text{NH} \cdot \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} - \text{O} \end{array}$, crystallises from benzene or chloroform in prisms, m. p. 99–100° (decomp.), and when boiled with absolute alcohol, yields phenylglycine anhydride, $\left(\text{CHPh} \begin{array}{c} \text{NH} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \right)_x$, as an amorphous powder insoluble in all ordinary solvents.

N-Carbomethoxyphenylalanine, $\text{CH}_2\text{Ph} \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{NH} \cdot \text{CO}_2\text{Me}$, is a syrup, and the corresponding phenylalanine-*N*-carboxylic anhydride,

$\text{CH}_2\text{Ph}-\text{CH} \begin{smallmatrix} \text{NH}\cdot\text{CO} \\ \diagup \quad \diagdown \\ \text{CO}\quad\text{O} \end{smallmatrix}$, crystallises from cold ethyl acetate in colourless, glistening, rectangular plates, m. p. 127—128°.

N-Carbomethoxyphenylalanine is a viscid oil, and *leucine-N*-carbomethoxy anhydride, $\text{C}_9\text{H}_{11}\text{O}_5\text{N}_2$, crystallises from benzene in colourless prisms, m. p. 48—50°. At above 80°, it loses carbon dioxide. J. J. S.

Amide Acids of Phenylsuccinic Acid. RICHARD ANSCHÜTZ and PAUL WALTER (*Annalen*, 1908, 361, 73—78).—It was found previously (Abstr., 1907, i, 766) that the action of ammonia or of substituted ammonias on phenylsuccinic anhydride leads to the formation of phenylsuccin- β -amic acids, $\text{CO}_2\text{H}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHR}$, the basic group combining with the carbonyl of the more feebly acid carboxyl. Lüttgen, on the other hand, on treating phenylsuccinic anhydride with ammonia, converting the resulting acid into the silver salt, and heating this with ethyl iodide, obtained small amounts of β -ethyl phenylsuccin- α -amate, $\text{NH}_2\cdot\text{CO}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, which he prepared also by the action of potassium cyanide on ethyl benzylidenemalonate and distillation of the resulting ethyl hydrogen β -carbamylbenzylmalonate, $\text{NH}_2\cdot\text{CO}\cdot\text{CHPh}\cdot\text{CH}(\text{CO}_2\text{Et})\cdot\text{CO}_2\text{H}$ (*Diss.*, Bonn, 1899). The comparison of these results made it appear probable that the action of ammonia on phenylsuccinic anhydride leads to the formation of a mixture of phenylsuccinamic acids, the β -amic acid being the chief product, and that Lüttgen's esterification product was a mixture of esters, from which he isolated only the more sparingly soluble isomeride. These views have now been confirmed.

β -Ethyl phenylsuccin- α -amate, prepared by the action of concentrated sulphuric acid on ethyl β -cyano- β -phenylpropionate, has m. p. 173° (167°: Lüttgen, *loc. cit.*).

When converted into the silver salt and heated with ethyl iodide at 50—60°, the product of the action of ammonia on phenylsuccinic anhydride yields chiefly α -ethyl phenylsuccin- β -amate together with small amounts of the β -ethyl α -amate. By converting the mixed amic acids into the corresponding methyl esters, which can be readily separated quantitatively, it is shown that only about 5% of the reaction product is the α -amic acid, the reaction of the anhydride with ammonia taking place to the extent of 95% according to the rule previously laid down. G. Y.

Wandering of Alkyl Groups During the Distillation of Ether Acids. JACQUES POLLAK and H. FELDSCHEK (*Monatsh.*, 1908, 29, 139—155).—Nitro-2:3:4-trimethoxybenzoic acid when distilled was found by Pollak and Goldstein (Abstr., 1907, i, 330) to be converted into the methyl ester of the acid. The object of this investigation was to ascertain whether the esterification of the acid depends on the presence of the nitro-group, and to what extent the change is influenced by the number and positions of the methoxy- and nitro-groups. The following substances were distilled under the ordinary and under reduced pressure: nitro-3:4:5-trimethoxybenzoic

acid, dinitroanisic acid, mononitroanisic acid, *o*:4:5-trimethoxybenzoic acid, *o*-methoxybenzoic acid, *m*-methoxybenzoic acid, and anisic acid. The results obtained may be summarised as follows: (1) The presence of a nitro-group in the molecule decreases the stability of the acid and favours the formation of the ester; thus, nitro-3:4:5-trimethoxybenzoic acid and dinitroanisic acid are largely converted into their methyl esters when distilled in a vacuum. (2) An increase in the number of nitro-groups is accompanied by a marked decrease in stability; thus, dinitroanisic acid decomposes with the formation of the methyl ester when distilled under a pressure of 12 mm., whilst nitroanisic acid is only partly converted into its ester when slowly distilled under a pressure of 40 mm. (3) The methoxy-acids which do not contain a nitro-group may be distilled in a vacuum without undergoing decomposition. *o*-Methoxybenzoic acid, when distilled under the ordinary pressure, decomposes, yielding a mixture of methyl salicylate and methyl *o*-methoxybenzoate. Anisic acid and, more especially, *m*-methoxybenzoic acid are far more stable than the ortho-compound. However, the methyl esters of these acids are also formed on heating them for several hours at 180—270°. (4) Since *o*-methoxybenzoic acid decomposes far more readily than 3:4:5-trimethoxybenzoic acid, it follows that the ortho-position of the groups has a greater influence on the stability of the compound than the presence of a large number of methoxy-groups not ortho to the carboxyl group. 3:4:5-Trimethoxybenzoic acid is, however, far less stable than either anisic or *m*-methoxybenzoic acid.

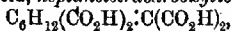
Ethyl 3:4:5-trimethoxybenzoate, $C_9H_2(OMe)_3 \cdot CO_2Et$, prepared by the action of methyl sulphate and potassium hydroxide on ethyl gallate, crystallises in white leaflets, m. p. 53—57°; the *nitro*-derivative, $NO_2 \cdot C_6H(OMe)_3 \cdot CO_2Et$, forms yellow crystals, m. p. 68—70°, and yields, on hydrolysis, the acid, $NO_2 \cdot C_6H(OMe)_3 \cdot CO_2H$, m. p. 164°.

W. H. G.

Santoninic Acid. ANGELO ANGELI and LUIGI MARINO (*Mem. R. Accad. Lincei*, 1908, [v], 6, 385—401. Compare *Abstr.*, 1907, i, 321).—The following oxidation products of santonin have been obtained by the authors.

Dioxysantonin, $C_{15}H_{13}O_8$, obtained by oxidising santonin in sodium hydroxide solution by means of permanganate, separates from benzene in crystals, m. p. 261°, reacts with phenylhydrazine or hydroxylamine, and is the lactone of a dioxysantoninic acid.

A syrupy *ketonic acid*, $CO_2H \cdot CO \cdot C_{10}H_{14}(CO_2H)(COMe) \cdot OH$, obtained in the same way as the preceding compound, yields a crystalline *phenylhydrazone*, $C_{15}H_{20}O_5(N_2HPh)_2$, m. p. about 100°, which behaves as a dibasic acid. When treated with lead dioxide, this ketonic acid loses carbon dioxide and yields another *ketonic acid*, which forms a *phenylhydrazone*, $C_{14}H_{20}O_5(N_2HPh)_2$, m. p. 114—116° (decomp). Under the action of alkaline permanganate solution, the syrupy ketonic acid, $C_{15}H_{20}O_7$, gives oxalic, formic, and acetic acids, together with an unstable acid, which readily loses two carbon atoms and forms a saturated aliphatic acid, *heptanetetra-carboxylic acid*,



m. p. 165° (decomp.). When the latter is heated, it loses water and carbon dioxide, yielding the *anhydride*, $C_7H_5(CO_2)_2 \cdot CO_2H$, m. p. 145° , of a heptanetricarboxylic acid. With water, this anhydride gives an acid, $C_{10}H_{15}O_8$, softening at about 88° , and then melting; with sodium hydroxide, the anhydride yields a *heptanetricarboxylic acid*, $C_{10}H_{15}O_8$, m. p. 127° . When the anhydride $C_{10}H_{15}O_8$ is oxidised with chromic and sulphuric acids, it yields succinic acid and a *pentanetricarboxylic acid*, $C_9H_5(CO_2H)_3$, m. p. about 110° , which may be identical with the acid prepared by Emery (Abstr., 1891, 547) and by Perkin (Trans., 1896, 69, 1510).

On heating a crude sample of the heptanetetracarboxylic acid, an *anhydride*, $C_{10}H_7O_8$, m. p. 141° , was obtained, which, when boiled with water, yields an acid, $C_{10}H_{13}O_8$, m. p. 141° .

T. H. P.

The Synthesis of Polypeptides. EMIL FISCHER (*Sitzungsber. K. Akad. Wiss. Berlin*, 1908, 542--553).—The methods employed in the synthesis of polypeptides from amino-acids are not directly applicable when it is required to combine aminohydroxy-acids, owing to the action of phosphorus pentachloride on the hydroxyl group. It is found that the introduction of the carbonethoxyl group gives the necessary protection, the group being afterwards readily removed by hydrolysis. The products are, however, optically inactive.

The reduction of polypeptides with sodium amalgam (this vol., i, 323) gives poor yields, but derivatives of acetals are readily prepared by condensing aminoacetal with chloroacetyl chlorides and treated the products with ammonia.

Chloroacetyl-L-tyrosine methyl carbonate,
 $CH_3Cl \cdot CO \cdot NH \cdot CH(CO_2H) \cdot CH_2 \cdot C_6H_4 \cdot O \cdot CO_2Me$,
 from chloroacetyl-L-tyrosine and methyl chlorocarbonate, separates from hot water as an oil, which slowly crystallises in thin, colourless, microscopic leaflets, m. p. 116° (corr.), $[\alpha]_D^{20} + 48.7^{\circ}$. It is readily hydrolysed by alkali.

With acetyl chloride and phosphorus pentachloride, it yields *chloroacetyltyrosyl chloride methyl carbonate*, which may be crystallised, but is best condensed, without previous isolation, with glycine ester, yielding *chloroacetyltyrosylglycine ester methyl carbonate*,

$CH_3Cl \cdot CO \cdot NH \cdot CH(CH_2 \cdot C_6H_4 \cdot O \cdot CO_2Me) \cdot CO \cdot NH \cdot CH_2 \cdot CO_2Et$,
 m. p. 130° (corr.), to a clear liquid, after sintering at 125° . The solutions in alcohol or chloroform are optically inactive. Sodium hydroxide hydrolyses it to *chloroacetyltyrosylglycine*,

$CH_3Cl \cdot CO \cdot NH \cdot CH(CH_2 \cdot C_6H_4 \cdot OH) \cdot CO \cdot NH \cdot CH_2 \cdot CO_2H$,
 which crystallises from hot water in small, quadrangular plates, m. p. $188-190^{\circ}$ (corr.) (decomp.).

Glycyltyrosylglycine, obtained by the action of ammonia on the above, separates from alcohol in microscopic crystals, m. p. 221° (corr.) (decomp.).

Glycylaminoacetal, $NH_2 \cdot CH_2 \cdot CO \cdot NH \cdot CH_2 \cdot CH(OEt)_2$, prepared from aminoacetal and chloroacetyl chloride and heating the chloro-compound thus obtained with aqueous ammonia at 100° or dissolving it in liquid ammonia, separates from light petroleum in deliquescent, colourless crystals, m. p. 45° . The base is strongly alkaline, and does

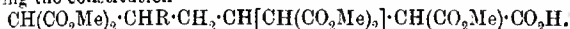
not reduce Fehling's solution. The *hydrochloride* forms microscopic leaflets, m. p. 119° (corr.) (decomp.). The *hydrogen oxalate*, prepared by precipitation in alcoholic solution, has m. p. about 150° (decomp.); the *picrate* crystallises from ethyl acetate in yellow needles. Cold hydrochloric acid converts glycyaminoacetal into glycyglycinaldehyde.

A form of capillary polarimeter tube is described, having a capacity of only 0.1 c.c., and a pycnometer of about the same capacity. It has been found possible to make satisfactory determinations of the rotatory power and density with 0.01—0.02 gram of the substance.

C. H. D.

Condensation Reactions of $\alpha\beta$ -Unsaturated Aldehydes. II.

HANS MEERWIN (*Annalen*, 1908, 360, 323—347. Compare this vol., i, 89).—Vorländer (Abstr., 1898, i, 27; 1905, i, 792) found that cinnamaldehyde and crotonaldehyde react readily with methyl sodiomalonate, whilst, on the other hand, Bechert (Abstr., 1894, i, 488) and Hinrichsen (Abstr., 1905, i, 132) prepared cyanocinnamylidenacetic esters and cinnamylidenemalononitrile by condensation of cinnamaldehyde with cyanoacetic esters and malononitrile respectively in presence of sodium ethoxide; hence it was to be expected that $\alpha\beta$ -unsaturated aldehydes would condense with methyl malonate in presence of sodium ethoxide to form products of the type $\text{CHR}:\text{CH}:\text{CH}:\text{C}(\text{CO}_2\text{Me})_2$. It is now found, however, that, in the presence of sodium ethoxide, methyl malonate reacts with 3 mols. of $\alpha\beta$ -unsaturated aldehyde, the product having the constitution



The mechanism of this reaction is discussed, and the conclusion is drawn that the first product is $\text{CH}(\text{CO}_2\text{Me})_2 \cdot \text{CHR} \cdot \text{CH}:\text{CH} \cdot \text{CH}(\text{CO}_2\text{Me})_2$, which, in presence of the alkali, may undergo transformation into $\text{CH}(\text{CO}_2\text{Me})_2 \cdot \text{CHR} \cdot \text{CH}_2 \cdot \text{CH}:\text{C}(\text{CO}_2\text{Me})_2$. The present paper contains an account chiefly of the derivatives of cinnamaldehyde.

Pentamethyl hydrogen α -phenylpropane- $\alpha\gamma\gamma$ -trimalonate, $\text{C}_{23}\text{H}_{28}\text{O}_{12}$, prepared from cinnamaldehyde and methyl malonate, crystallises in flat needles, m. p. 119 — 120° , loses 1 mol. of carbon dioxide at 140 — 150° , and slowly decolorises permanganate, but not bromine. The *polycarboxylic acid*, obtained on hydrolysis of the ester with dilute sodium hydroxide, is an oil. *Methyl α -phenylpropane- $\alpha\gamma\gamma$ -trimalonate*, $\text{C}_{21}\text{H}_{26}\text{O}_{12}$, prepared from methyl cinnamylidenemalonate and methyl malonate, or by esterification of the pentamethyl hydrogen ester by means of methyl alcohol and hydrogen chloride, crystallises in monoclinic prisms, m. p. 86 — 87° .

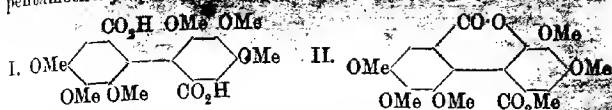
Knoevenagel and Herz's supposed methyl cinnamylidenemalonate (Abstr., 1905, i, 63), prepared by the action of cinnamaldehyde on methyl malonate in piperidine solution, is now found to be methyl cinnamylidenemalonate, m. p. 67° (Thiele and Meisenheimer, Abstr., 1899, i, 603).

β -Phenylpimelic- δ acetic acid,



is formed together with smaller amounts of 1-phenylcyclohexane-3-one-5-acetic acid when the pentamethyl hydrogen ester is boiled with

methyl ester, and the lactone of methyl 2-hydroxy-3:4:4':5':6'-pentamethoxydiphenyl-6:2'-dicarboxylate (II).



In carrying out methoxyl determinations with these substances, it was found necessary to add repeatedly small portions of strong hydriodic acid, and to boil until methyl iodide ceased to be evolved; this often required seven to fourteen hours.

Tetramethylellagic acid is readily prepared by acting on ellagic acid with an ethereal solution of diazomethane (compare Goldschmiedt, Abstr., 1905, i, 900). It is converted into a mixture of methyl 2:3:4:4':5':6'-hexamethoxydiphenyl-6:2'-dicarboxylate and of the lactone of methyl 2-hydroxy-3:4:4':5':6'-pentamethoxydiphenyl-6:2'-dicarboxylate when boiled for sixteen hours with methyl iodide and potassium hydroxide in alcoholic solution.

Methyl 2:3:4:4':5':6'-hexamethoxydiphenyl-6:2'-dicarboxylate, $C_{12}H_2(OMe)_6(CO_2Me)_2$, crystallises in two forms: small, coarse crystals, m. p. 109—111°, and slender, white needles, m. p. 90—95°. It is hydrolysed when boiled with an alcoholic solution of potassium hydroxide, yielding the *ether acid*, $C_{12}H_2(OMe)_6(CO_2H)_2$, m. p. 240°. Both the ether acid and its methyl ester are converted by hydriodic acid into ellagic acid.

The *lactone of methyl 2-hydroxy-3:4:4':5':6'-pentamethoxydiphenyl-6:2'-dicarboxylate*, $C_{12}H_2O_2(OMe)_5 \cdot CO_2Me$, m. p. 109—111°, when hydrolysed with alcoholic potassium hydroxide, is converted into *2-hydroxy-3:4:4':5':6'-pentamethoxydiphenyl-6:2'-dicarboxylic acid*, $OH \cdot C_{12}H_2(OMe)_5(CO_2H)_2$, m. p. 200—203° (decomp.). The latter compound, when treated with diazomethane, yields the above mentioned methyl hexamethoxydiphenyldicarboxylate.

Preparation of Ellagic Acid [with MARIANNE VON BRONNECK].—The accuracy of Ernst and Zwenger's statement (*Annalen*, 1869, 159, 32) that ellagic acid is formed on treating ethyl gallate with sodium carbonate or ammonia in the presence of air seemed doubtful, since gallic acid when treated with potassium hydroxide yields galloflavin; their work was therefore repeated, and found to be correct. Ellagic acid is also formed from methyl gallate in the same way. Details are given for obtaining the best yield of ellagic acid from ethyl gallate.

W. H. G.

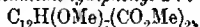
Resoflavin and its Analogue from Gallic Acid. JOSEF HERZIG and RUDOLF TSCHERNE (*Monatsh.*, 1908, 29, 281—294. Compare Perkin and Nierenstein, *Trans.*, 1904, 87, 1412).—A continuation of work previously published (Abstr., 1907, i, 421). When the ether ester, $C_{14}H_3O_2(OMe)_7$, obtained from resoflavin is heated with a dilute potassium hydroxide solution, it is converted into the ether acid, $CO_2H \cdot C_{12}H_3(OMe)_5 \cdot CO_2Me$ (*loc. cit.*), but when heated with strong aqueous potassium hydroxide it yields the ether acid, $C_{12}H_3(OMe)_5(CO_2H)_2$.

Since resorflavin when heated with zinc dust yields fluorone, it is evidently a derivative of diphenyldimetholide; two of the hydroxyl groups probably occupy positions 4 and 4' in the diphenyl nucleus, but the position of the third is still uncertain.

The analogue of resorflavin obtained from gallic acid by oxidation with ammonium persulphate is shown to be a monohydroxyellagic acid having the annexed constitution, since it is converted into the ether ester, $C_{14}H_3O_2(OMe)_7$, when treated with potassium hydroxide and methyl iodide; the ether ester on hydrolysis yields the ether acid, $C_{12}H(OMe)_7(CO_2H)_2$.

[With S. EPSTEIN.]—The ether ester, $C_{14}H_3O_2(OMe)_7$ (Herzig and Tscherne, *loc. cit.*), when boiled with a strong solution of potassium hydroxide in dilute alcohol, is converted into 3 (or 5) : 2 : 4 : 4' : 6'-pentamethoxydiphenyl-6 : 2-dicarboxylic acid, $C_{12}H_3(OMe)_5(CO_2H)_2$, crystallising in white needles, m. p. 247—249°.

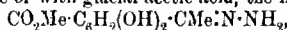
[With MARIANNE VON BRONNECK.]—The product obtained by the oxidation of gallic acid with persulphate (flavellagic acid) is converted by diazomethane into the ether ester, $C_{14}H_3O_2(OMe)_7$, m. p. 245°. It is converted by methyl iodide and potassium hydroxide into methyl 3 : 4 : 5 : 6 : 2' : 3' : 4'-heptamethoxydiphenyl-2 : 6'-dicarboxylate,



m. p. 83—87°, which, on hydrolysis with potassium hydroxide, yields the acid, $C_{12}H(OMe)_7(CO_2H)_2$, m. p. 163—167°; it crystallises with $1H_2O$, and then has m. p. 95—100° (decomp.). W. H. G.

Glaucohydroellagic Acid. MAXIMILIAN NIERENSTEIN (*Ber.*, 1908, 41, 1649—1650).—With the object of ascertaining whether ellagic acid on reduction behaves like tannin (compare Nierenstein, this vol., i, 90), the formation of glaucohydroellagic acid from ellagic acid has been investigated (compare Rembold, this Journ., 1876, i, 592). It is found that glaucohydroellagic acid is identical with pentahydroxydiphenyl-methylolide, described by A. G. Perkin and Nierenstein (*Trans.*, 1905, 87, 1420). W. H. G.

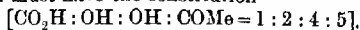
Xanthophanic Acid. IV. f CARL LIEBERMANN and SIMON LINDENBAUM (*Ber.*, 1908, 41, 1607—1619. Compare Abstr., 1906, i, 556; 1907, i, 889).—It was shown previously that the bromophenyl-hydrazone prepared from the "transformation product" of xanthophanic acid is a derivative, not of this, but of methyl resacetophenone-carboxylate. This is now found to be the case also with the hydrazone formed by the action of hydrazine on the "transformation product." When heated alone or with glacial acetic acid, the hydrazone,



yields hydrazine and a lemon-yellow compound, which must have the constitution $N_2[CMe \cdot C_6H_3(OH)_2 \cdot CO_2Me]_2$, as when boiled with dilute sulphuric acid it forms hydrazine, methyl alcohol, and resacetophenone. These substances have now been prepared synthetically.

Resorcinol dimethyl ether is converted by means of hydrogen cyanide and hydrochloric acid into β -resorcylaldehyde dimethyl ether,

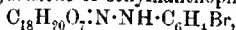
which is oxidised by potassium permanganate, forming β -resorcylic acid dimethyl ether, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3(\text{OMe})_2$ ($\text{EO}_2\text{H}:\text{OMe}:\text{OMe}=1:2:4$). An acetyl group is introduced into this by means of acetyl chloride and aluminium chloride, and finally the methyl groups are removed by treatment with hydriodic acid. This series of changes has been carried out also, starting from resorcinol diethyl ether. The resulting acid is identical with resacetophenonecarboxylic acid, which is obtained from the "transformation product" of xanthophanic acid methyl or ethyl ether, and must have the constitution



The methyl ester of the synthetical acid yields a *p*-bromophenylhydrazone identical with that obtained from the "transformation product." On the other hand, the hydrazone obtained from the synthetical methyl ester differs from that prepared from the "transformation product" both in its m. p. and in its solubility. It is considered that these hydrazones may be stereoisomerides, the more that the lemon-yellow products obtained on heating the hydrazones are identical.

When heated with ethyl ethoxymethyleneacetoacetate and small amounts of sodium ethoxide in alcoholic solution, ethyl resacetophenonecarboxylate yields traces of xanthophanic and glaucophanic acids, but the chief product is an acid, $\text{C}_{16}\text{H}_{14}\text{O}_7$, which crystallises in needles, m. p. $164-165^\circ$.

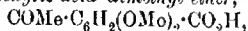
The *p*-bromophenylhydrazone of ethylxanthophanic acid,



prepared from ethylxanthophanic acid and *p*-bromophenylhydrazine in benzene solution, crystallises in red needles, m. p. $180-181^\circ$, decomposes on prolonged boiling with alcohol, and gives a yellowish-green fluorescence with concentrated sulphuric acid.

The products of each stage of the synthesis of resacetophenonecarboxylic acid were isolated and are described. The following are new.

Resacetophenonecarboxylic acid dimethyl ether,



crystallises in prisms, m. p. $231-233^\circ$. The diethyl ether, m. p. $190-202^\circ$, was obtained mixed with the monoethyl ether.

Methyl resacetophenonecarboxylate crystallises in needles, m. p. 124° . The ethyl ester, colourless needles, m. p. 94° . The *p*-bromophenylhydrazone of the methyl ester, m. p. $227-228^\circ$ (224° : *loc. cit.*).

The hydrazone, prepared by the action of hydrazine on the "transformation product" of ethylxanthophanic acid, crystallises in white needles, m. p. 138° , decomp. $150-160^\circ$, forming the lemon-yellow azine, $\text{C}_{30}\text{H}_{20}\text{O}_8\text{N}_2$, m. p. 327° . The hydrazone, obtained from the synthetical methyl ester, forms yellowish-green crystals, m. p. 170° , changing into the lemon-yellow azine, m. p. 327° .

G. Y.

Condensation of *o*-Nitrobenzaldehyde with Aromatic Hydrocarbons in Presence of Concentrated Sulphuric Acid. ALFRED KLIEGL (*Ber.*, 1903, 41, 1845-1851. Compare this vol., i, 82).—*m*- and *p*-Nitrobenzaldehyde condense with benzene in presence of concentrated sulphuric acid to form *m*- and *p*-nitrotriphenylmethane (Baeyer and

Tschacher, Abstr., 1887, 44, 1888, 373; 1890, 1141), but the author finds that the reaction proceeds quite differently when *o*-nitrobenzaldehyde is used, *o*-nitrophenyl *p*-tolyl ketone and *p*-tolylanthroxan being obtained from toluene, and phenylanthroxan with but a trace of *o*-nitrobenzophenone (in one experiment) from benzene. To confirm these results, *o*-nitrophenyl *p*-tolyl ketone was synthesised by oxidising *o*-nitrophenyl-*p*-tolylmethane (yellow oil, b. p. 195–198°/12 mm., prepared from *o*-nitrobenzyl chloride and toluene in presence of aluminium chloride) with sodium dichromate and glacial acetic acid. It forms thin, colourless prisms, m. p. 155°. On oxidation, it yields 2'-nitro-4-benzoylbenzoic acid, shining plates, m. p. 235·5–236°, and on reduction with tin and glacial acetic acid, *p*-tolylanthroxan, $C_{11}H_{11}ON$, yellow crystals, m. p. 95·5°.

The Reaction between Potassium Cyanide and *o*-Nitrobenzaldehyde. JOAN POPOVICI (*Ber.*, 1908, 41, 1851–1853).—By the interaction of potassium cyanide and *o*-nitrobenzaldehyde, the author obtained (Abstr., 1907, i, 628) 2:2'-dinitrobenzoin, but Ekecrantz and Ahlquist (this vol., i, 347) stated that the product of the reaction was a mixture of *o*-nitrosobenzoic acid and *o*-azoxybenzoic acid. The author has now repeated the experiment under the same conditions, and confirms the former result. 2:2'-Dinitrobenzoin has m. p. 161–162° (corr.), and not 155·5° (corr.) as previously given. J. C. C.

Synthesis of Pulenone Derivatives from *o*-Cresol. KARL AUWERS and MAX HESSENLAND (*Ber.*, 1908, 41, 1790–1816).—The product, $C_9H_{12}OCl_2$ (Abstr., 1906, i, 947), obtained by the action of magnesium methyl iodide on 2-keto-1-methyl-1-dichloromethyl- Δ^5 -cyclohexadiene, is shown to be a ketone, although it gives none of the characteristic reactions of ketones, probably owing to the inhibiting effect of the $-CHCl_2$ group. When reduced for several days with acetic acid and zinc dust, it yields the ketone, $C_9H_{14}O$, in the form of a liquid, b. p. 63–65°/16 mm. or 172–174°/757 mm., with an odour of peppermint.

The corresponding semicarbazone, $C_{10}H_{17}ON_3$, crystallises from a mixture of benzene and light petroleum in glistening needles, m. p. 129°. The ketonic nature of these products indicates that the magnesium methyl iodide has added itself to the double bond, and not to the carbonyl group, so that the original condensation product is 1:4-dimethyl-4-dichloromethyl- Δ^5 -cyclohexen-3-one, and the reduction product, 1:4:4-trimethyl- Δ^5 -cyclohexen-3-one or β -pulenone, $CH<CH-CMe_2>CO$ (compare Wallach, 1904, i, 74).

The optical properties of the compounds are in complete harmony with these formulae. When reduced with sodium and alcohol, β -pulenone yields an unsaturated alcohol, β -pulenol, $C_9H_{16}O$, as a clear, mobile liquid, b. p. 82–85°/15 mm. or 189°/754 mm. It has D_{20}^{25} 0·9209 and n_D^{25} 1·47398, and when oxidised with chromic anhydride yields β -pulenone.

The product obtained by the action of concentrated sulphuric acid on dichloro- β -pulenone is the isomeric dichloro- α - β -pulenone,

$\text{CH}_2 < \begin{smallmatrix} \text{CH}_2 - \text{CMe}(\text{CHCl}) \\ \text{CMe}(\text{OH}) - \text{CH}(\text{OH}) \end{smallmatrix} > \text{CO}$ (compare Abstr., 1906, I, 947), and when reduced with acetic acid and zinc dust yields $\alpha\beta$ -pulenone as an oil, b. p. $86-88^\circ/15$ mm. or $208^\circ/753$ mm. It has D_4^{20} 0.9317 and n_D^{20} 1.47958. Its semicarbazone crystallises from methyl alcohol in flat, glistening prisms, m. p. $200-201^\circ$. When reduced, the $\alpha\beta$ -ketone yields a saturated alcohol, pulenol, probably identical with Wallach's pulenol, as when oxidised it yields pulenone. The formation of this saturated alcohol is in harmony with the view that $\alpha\beta$ -pulenone has the ethylene linking in the $\alpha\beta$ -position with respect to the carbonyl group. An examination of the oxidation products also supports this view. When oxidised with permanganate at $0-10^\circ$, $\alpha\beta$ -pulenone yields a mixture of Wallach's *aa*-dimethyl- γ -acetylbutyric acid, the semicarbazone of which has m. p. 169° (Wallach: 163°), and *aa\delta*-trimethyl- δ -hydroxyadipic acid, m. p. $145-148^\circ$, which is insoluble in benzene. A bimolecular reduction product, $\text{C}_{18}\text{H}_{26}\text{O}_2\text{Cl}_2$, is obtained when dichloro- $\alpha\beta$ -pulenone is reduced with sodium amalgam, alcohol, and dilute acetic acid; a small amount is also formed during the reduction with zinc dust and acetic acid. It crystallises from alcohol, and has m. p. $215-225^\circ$.

Dichloro- $\alpha\beta$ -pulenone reacts with magnesium methyl iodide, yielding 1:1:4-trimethyl-4-dichloromethylcyclohexan-3-one, $\text{C}_{10}\text{H}_{16}\text{OCl}_2$, which has h. p. $135-145^\circ/17-18$ mm., m. p. 73° .

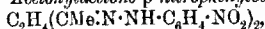
Dihydroxydichloropulenone (1:2-dihydroxy-1:4-dimethyl-4-dichloromethylcyclohexan-3-one), $\text{CH}_2 < \begin{smallmatrix} \text{CH}_2 - \text{CMe}(\text{CHCl}) \\ \text{CMe}(\text{OH}) - \text{CH}(\text{OH}) \end{smallmatrix} > \text{CO}$, is formed when dichloro- $\alpha\beta$ -pulenone is oxidised with a dilute aqueous acetone solution of permanganate in the presence of acid. It crystallises from water in compact prisms containing $1\text{H}_2\text{O}$; it melts at 70° , then solidifies, and melts again at 113° . Its monobenzoyl derivative, $\text{C}_{10}\text{H}_{16}\text{O}_4\text{Cl}_2$, has m. p. $182-183^\circ$. J. J. S.

Conversion of Dichloro- $\alpha\beta$ -pulenone into $\Delta^{1,3}$ -Dihydro-*p*-xylene. KARL AUWERS and MAX HESSENLAND (*Ber.*, 1908, 41, 1816-1827).—When dichloro- $\alpha\beta$ -pulenone (preceding abstract) is warmed with alcoholic potash, the chief products are a monobasic unsaturated acid, $\text{C}_9\text{H}_{13}\text{O}_2\text{Cl}$, an unsaturated acid, $\text{C}_9\text{H}_{12}\text{O}_2$, and a hydrocarbon, C_8H_{12} . The chlorinated acid is formed in small quantities only, probably according to the equation $\text{C}_9\text{H}_{12}\text{OCl}_2 + \text{H}_2\text{O} \rightarrow \text{C}_9\text{H}_{13}\text{O}_2\text{Cl} + \text{HCl}$; it crystallises from light petroleum, has m. p. 141.5° , and is probably 3-chloro-1:4-dimethyl- Δ^1 -cyclohexene-2-carboxylic acid. The acid $\text{C}_9\text{H}_{12}\text{O}_2$ can be obtained in larger quantity, and is 1:4-dimethyl- $\Delta^{1,3}$ -cyclohexadiene-2-carboxylic acid. It is best purified by conversion into the methyl ester and subsequent hydrolysis with alcoholic potassium hydroxide. The acid crystallises from dilute methyl alcohol or from light petroleum in glistening, flat plates, m. p. $40-42^\circ$. It is volatile with steam, but when heated alone to $155-175^\circ$, or when boiled with oxalic acid solution or with alkalis, carbon dioxide is eliminated and the hydrocarbon C_8H_{12} formed. The acid combines with bromine, and the dibromide when heated with alcoholic potassium hydroxide yields 2:5-dimethylbenzoic acid. The

methyl ester, $C_{10}H_{14}O_2$, has b. p. $79-81^\circ/10$ mm., D_4^{20} 0.997, n_D^{18} 1.47643, and it is only slowly polymerised.

$\Delta^{1,3}$ -Dihydro-*p*-xylene (1:4-dimethyl- $\Delta^{1,3}$ -cyclohexadiene) is a clear, mobile liquid with an ethereal odour. It has D_4^{20} 0.832, n_D^{18} 1.478.

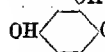
The hydrocarbon yields a dihydromide, m. p. $240-247^\circ$, and when nitrated yields trinitro-*p*-xylene. The constitution of the hydrocarbon follows from the formation of this nitro-derivative, and from the fact that acetylacetone and acetone are found among its products of oxidation. The two ketones were isolated in the form of their *p*-nitro-phenylhydrazones. Acetylacetone *p*-nitrophenylhydrazone,

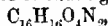


crystallises from glacial acetic acid or boiling amyl alcohol, and has m. p. $210-212^\circ$.

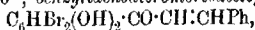
J. J. S.

Derivatives of Resacetophenone. WILLY DAHSE (*Ber.*, 1908, 41, 1619-1625).—The compounds described were prepared in order to compare them with the resacetophenone derivatives obtained from xanthophanic acid (compare this vol., i, 548). Resacetophenonehydrazone,

OH  CMe:N·NH₂, obtained by the action of hydrazine hydrate on the ketone in absolute alcohol, crystallises in white needles; on boiling with glacial acetic acid or heating at 125° , the azine,



is formed, crystallising from nitrobenzene in yellow needles, m. p. 307° . Resacetophenone gives only a monoacetate on boiling with sodium acetate and acetic anhydride (m. p. $72-73^\circ$, Nencki and Sieber, *Abstr.*, 1881, 591), the phenylhydrazone, $C_{16}H_{16}O_3N_2$, of which forms golden-yellow needles, m. p. 130° . Bromination of resacetophenone gives 3:5-dibromoresacetophenone, $C_6HBr_2(OH)_2 \cdot COMe$, crystallising in needles, m. p. $173-174^\circ$; the hydrazone, $C_8H_8O_2N_2Br_2$, forms glistening, white needles, and at 145° or on heating with glacial acetic acid passes into the azine, $C_{16}H_{12}O_4N_2Br_4$, yellow needles, m. p. 340° ; the phenylhydrazone, $C_{11}H_{12}O_2N_2Br_2$, crystallises in white needles, m. p. 162° . Benzylidene derivatives are obtained on heating the dibromoresacetophenone with the aldehyde and concentrated sulphuric acid at 100° ; benzylidenedibromoresacetophenone,

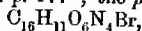


forms greenish-yellow needles, m. p. 165° ; the *m*- and *p*-nitrobenzylidene derivatives, $C_{15}H_9O_2NBr_2$, are greenish-yellow, and have m. p. 236° (decomp.) and 228° respectively.

Dibromoresacetophenone diacetate, $C_{12}H_{10}O_6Br_2$, crystallises from alcohol in needles, m. p. $104-105^\circ$, and on oxidation with chromic acid in acetic acid gives 3:5-dibromo-2:4-dihydroxybenzoic acid (Zehenter, *Abstr.*, 1882, 193), a result which establishes the position of the bromine atoms in dibromoresacetophenone.

Bromodinitrodihydroxybenzoic acid, $C_6Br(NO_2)_2(OH)_2 \cdot CO_2H$, obtained when dibromoresacetophenone is warmed with three times its weight of nitric acid (D 1.4), crystallises from water in yellow needles, m. p. 187° ; the silver salt, $C_7H_2O_6N_2BrAg$, is an unstable, orange-yellow powder; the methyl ester, $C_8H_6O_6N_2Br$, forms white needles, m. p. 100° .

When, however, the dibromoresacetophenone is kept cool during nitration, bromodinitroresacetophenone, $C_8H_5O_2N_2Br$, is formed, which crystallises in yellowish-white needles, m. p. 148° ; the potassium and sodium salts are golden-yellow; the diacetate, $C_{12}H_9O_6N_2Br$, crystallises in white needles, m. p. 177° ; the phenylhydrazone,



in red needles, m. p. 236° ; the hydrazone, $C_8H_7O_6N_4Br$, in brown needles, decomp. 161° ; the azine, $C_{16}H_{10}O_{12}N_6Br_2$, is yellow, m. p. 320° . W. R.

1:5-Diketones. III. PAUL RABE (*Annalen*, 1908, 360, 265—288. Compare Abstr., 1904, i, 747).—The author has continued his work on the synthesis of dicyclic keto-alcohols containing a bridged linking by transformation of semi-cyclic 1:5-diketones.

Transformation of Ethyl γ -Benzoyl- α -acetyl- β -diphenylbutyrate into a Cyclic Keto-alcohol [With RICHARD EHRENSTEIN].—When deoxybenzoin is condensed with ethyl benzylidenecacetoacetate in presence of sodium ethoxide, the sodium compound of ethyl γ -benzoyl- α -acetyl- β -diphenylbutyrate is obtained, which, on treatment with ice-cold dilute sulphuric acid, yields the ester as a pale yellow, viscous oil, giving a violet coloration with alcoholic ferric chloride. This, slowly when alone, or more rapidly by treatment with alcohol, is transformed into ethyl 1:2:3-triphenylcyclohexan-1-ol-5-one-4-carboxylate, m. p. 123° , alcoholic solutions of which, when freshly prepared, do not give a reaction with ferric chloride, but when boiled for some time give a violet coloration. The substance therefore, on boiling, is partly converted into an enolic modification; this is obtained as a viscous oil by treating the sodium derivative with dilute sulphuric acid. It is quickly converted into the ketonic form in presence of alcohol. Ethyl 2:3:4-triphenyl-1:6-dimethyl-1:4-dihydropyridine-5-carboxylate, obtained by mixing the sodium compound of ethyl γ -benzoyl- α -acetyl- β -diphenylbutyrate with methylamine hydrochloride in alcoholic methylamine solution, has m. p. 88° . Ethyl 5-methylimino-1:2:3-triphenylcyclohexan-1-ol-4-carboxylate, m. p. 108° , results on mixing ethyl 1:2:3-triphenylcyclohexan-1-ol-5-one-4-carboxylate with alcoholic methylamine.

Dicyclic Alcohols with Bridged Linkings [With MAX JAHR].—Methyldicyclononanolone (Abstr., 1904, i, 509), on treatment with hydroxylamine, furnishes two stereoisomeric oximes. The α -oxime, which separates on pouring the mixture on to ice, has m. p. 201° , and contains benzene of crystallisation when crystallised from this solvent. On reduction with sodium and alcohol, it yields the corresponding α -amine, m. p. 202 — 204° . The β -oxime, isolated from the mother liquor, has m. p. 145° , and on reduction furnishes the β -amine, m. p.

86— 87° . Both these amines have the common position of a 7-amino-1-methyldicyclo-[1:3:3]-nonan-5-ol (annexed formula). The β -amine forms a hydrochloride, m. p. 272 — 275° (decomp.), a yellow picrate, decomp. 238° , a picrolonate, decomp. 285 — 286° , and a methiodide, decomp. 278° .

1:3-Dimethyldicyclo-[1:3:3]nonan-5-ol-*Y*me, obtained by condensing dimethylcyclohexanone and ethyl acetate in presence of sodium ethoxide, has m. p. 85°, and b. p. 160—170°/9—10 mm. On reduction with sodium and alcohol, it gives 1:3-dimethyldicyclo-[1:3:3]nonan-5:7-diol, m. p. 195°, and on treatment with hydriodic acid and phosphorus, 1:3-dimethyldicyclo-[1:3:3]nonane, a colourless, volatile liquid, b. p. 195—200°/750 mm. Dimethyldicyclononanone forms an α -oxime, m. p. 186—187°, and a β -oxime, m. p. 140—141°. The former gives the corresponding α -amine, m. p. 203—204°, and the latter the β -amine, m. p. 155°. The hydrochloride, decomp. at 265—268°, the picrate, m. p. 225—227° (decomp.), the picrolonate, decomp. at 274—275°, and the methiodide, decomp. at 220—223°, of the latter were prepared. J. C. C.

Method for the Determination of the Configuration of α -Dioximes. LEO TSCHUGAEFF (*Ber.*, 1908, 41, 1678—1684. Compare Abstr., 1905, i, 743).—The fact that, of the various stereoisomerides of an α -dioxime, the *syn*-modification alone yields complex metallic dioximines is utilised for the determination of the configuration of dioximes. Stierlin's α -anisildioxime (Abstr., 1889, 512), Hoffmann's α -cuminildioxime (Abstr., 1890, 1143), and α -furildioxime (m. p. 166—168°) are thus shown to possess the *syn*-configuration, whilst Werner and Bloch's two stereoisomeric *o*:*o*'-dichlorobenzildioximes (Abstr., 1899, i, 753), which do not form coloured complex metallic derivatives, must be the *amphi*- and the *anti*-modifications.

An interesting illustration of the method is given by Boeris stereoisomeric methylanisylglyoxaldioximes (Abstr., 1894, i, 72). The modification, m. p. 125°, obtained by Angeli's method of reducing the corresponding peroxide, is probably the *amphi*-dioxime, and, in accordance with the rule, does not form dioximines. By heating, it is transformed into an isomeride, m. p. 207°, which does yield dioximines, and has consequently the *syn*-configuration, although Angeli's researches on purely aromatic peroxides show that the *amphi*-dioximes obtained by reduction are converted into *anti*-dioximes by heat. An explanation is offered of the abnormal behaviour of the preceding aliphatic aromatic dioxime. The nickel and the ferrodipyrindine dioximines of α -anisildioxime and of α -furildioxime are described shortly. C. S.

Diethoxybenzoquinone. JACQUES POLLAK and J. GOLDSTEIN (*Monatsh.*, 1908, 29, 135—138).—Will has stated (Abstr., 1883, 457) that some dimethoxybenzoquinone is formed on adding pyrogallol trimethyl ether to concentrated nitric acid, whilst according to Schiffer (Abstr., 1892, 715) pyrogallol triethyl ether is not converted into diethoxybenzoquinone when added to nitric acid in glacial acetic acid.

This difference in the behaviour of the two ethers has been further investigated. Schiffer's work has been repeated and confirmed; when, however, the trimethyl ether is treated in the same way, it is partly converted into dimethoxybenzoquinone. It is also found that if the mixture of nitric and glacial acetic acids is added to a solution of pyrogallol triethyl ether in glacial acetic acid, some diethoxybenzoquinone is formed. The latter compound crystallises in wide

needles, m. p. 124—126° (compare Weidel and Pollak, *Abstr.*, 1900, i, 290).

Bornyl Palmitate. O. VON SOBBER (*J. pr. Chem.*, 1908, [ii], 77, 510—512).—Bornyl palmitate is best prepared by the action of palmityl chloride, which has been distilled over sodium, on the sodium derivative of borneol in boiling ethereal solution. The borneol should first be freed from isoborneol by the alcohol-sulphuric acid method. The ester crystallises in glistening, white scales, m. p. 67—68°.

G. Y.

Preparation of Acetals by Claisen's Method. ALEXANDER E. ARBUSOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 637—652).—Part of this paper has been already published (*Abstr.*, 1907, i, 749).

The action of ethyl orthoformate on menthone or pulegone in presence of sulphuric acid yields the unstable acetal of menthone or pulegone, which, under the conditions of experiment, decomposes, giving ordinary alcohol and the ether corresponding with an unsaturated alcohol. Thus menthone yields the *ether*, $C_{10}H_{17} \cdot OEt$, b. p. 83—84°/9 mm., D_4^{20} 0.8749, and pulegone the *ether*, $C_{10}H_{15} \cdot OEt$, b. p. 97—97.5°/12 mm., D_4^{20} 0.9047.

Camphoracetal, $C_{10}H_{16}(OEt)_2$, prepared by the action of ethyl orthoformate on camphor in presence of sulphuric acid, is an almost colourless liquid, b. p. 119—120°/16.5 mm., D_4^{20} 0.9632, D_4^{20} 0.9462. Besides camphoracetal, this reaction gives a *compound*, b. p. 82—83°/15 mm., which contains C, 72.73% and H, 10.62%, and is probably a compound of camphor and alcohol analogous with the so-called chloral alcoholate.

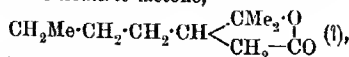
Methylmenthone, $C_{11}H_{20}O$, prepared by the action of magnesium methyl iodide on menthone, is a colourless, pleasant-smelling liquid, b. p. 103°/17 mm., 215.5°/749.6 mm., D_4^{20} 0.9121, D_4^{20} 0.8970.

T. H. P.

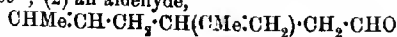
Chemical Action of Light. XII. GIACOMO L. CIAMICIAN and PAUL SILBER (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 576—582; *Ber.*, 1908, 41, 1928—1935. Compare *Abstr.*, 1907, i, 587; this vol., i, 277).—When dissolved in aqueous alcohol and subjected to the prolonged action of light, dihydrocarvone, like other *cycloketones* (*loc. cit.*), yields an aliphatic acid and an aldehyde, whilst carvone is almost completely converted into an isomeric compound under the same conditions.

The products yielded by dihydrocarvone are (1) the *acid*,

$CH_3Me \cdot CH_2 \cdot CH_2 \cdot CH(CMe \cdot CH_2) \cdot CH_2 \cdot CO_2H$ (1), which is an oily liquid, b. p. 135—137°/12 mm., 254.5°/758 mm., and, when boiled with sulphuric acid diluted with its own volume of water, is transformed into the *isomeric lactone*,



b. p. 264—265°; (2) an aldehyde,



which was not separated, but was converted into the corresponding hydroxamic acid, and this, by boiling with aqueous sulphuric acid, into the lactone, $\text{CHMe} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CH} \begin{smallmatrix} \text{CM}_2 \cdot \text{O} \\ \text{CH}_2 \cdot \text{CO} \end{smallmatrix}$, b. p. 266—267°.

Carvone yields (1) an isomeric compound (annexed formula), m. p. 100°, b. p. 206.5°, which has the normal molecular weight in freezing acetic acid and (2) closely resembles camphor in odour and appearance; its oxime, $\text{C}_{10}\text{H}_{14}\text{ON}$, m. p. 126—128°, separates from light petroleum in large, monoclinic crystals [Boeris: $a:b:c = 1.1057:1:0.6233$; $\beta = 67^\circ 36'$], and its semicarbazone, $\text{C}_{11}\text{H}_{17}\text{ON}_3$, crystallises from alcohol in large prisms, m. p. 239°; (2) a small proportion of an oily compound, $\text{C}_{10}\text{H}_{16}\text{O}$ or $\text{C}_{10}\text{H}_{15}\text{O}$, b. p. 218—223°, which has an odour resembling that of roses.

T. H. P.

Action of Magnesium Methyl Iodide on Carvenone and Pulegone. HANS RUPE and F. EMMERICH (*Ber.*, 1908, 41, 1750—1754).—The action of magnesium methyl iodide on carvenone,

$\text{CHMe} \begin{smallmatrix} \text{CO} \cdot \text{CH} \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} > \text{CPr}^\beta$, leads to the formation of an unstable, tertiary alcohol, which loses water, forming an unsaturated hydrocarbon, which must be 2-methylcarvenene, $\text{CMe} \begin{smallmatrix} \text{CMe} \cdot \text{CH} \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} > \text{CPr}^\beta$,

since its molecular refraction is considerably higher than the calculated, as is also that of carvenone. It has been shown by other authors (Wallach, *Abstr.*, 1895, i, 672; 1904, i, 752; 1905, i, 450; Knoevenagel, *Abstr.*, 1897, i, 606) that in regard to their molecular refractions, $\alpha\beta$ -unsaturated ketones resemble alcohols with two ethylene linkings. The high molecular refraction of the unsaturated hydrocarbon agrees with the presence of two conjugated ethylene linkings. The hydrocarbons obtained in the same manner from carvone, dihydrocarvone, pulegone, and isopulegone (this vol., i, 433), which contain an ethylene linking in the 4(8)- or (8)(9)-position, have normal refractions, and hence cannot contain conjugated ethylene linkings.

The hydrocarbon obtained by the action of methyl iodide on pulegone, $\text{CHMe} \begin{smallmatrix} \text{CH}_2 \cdot \text{CO} \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} > \text{C} \cdot \text{CMe}_2$, must be 3-methyl- $\Delta^{4(9)}$ -menthadiene, $\text{CMe} \begin{smallmatrix} \text{CH} \cdot \text{CHMe} \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} > \text{C} \cdot \text{CMe}_2$, and not 3-methylene- $\Delta^{4(9)}$ -terpene, $\text{CHMe} \begin{smallmatrix} \text{CH}_2 \cdot \text{C}(\text{CH}_2) \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} > \text{C} \cdot \text{CMe}_2$, as stated by Grignard (*Abstr.*, 1901, i, 679).

2-Methylcarvenene, $\text{C}_{11}\text{H}_{18}$, is a colourless, mobile oil, b. p. 86—87°/10 mm., $D_{20}^{20} 0.8563$, $n_D^{20} 1.49613$, $[\alpha]_D^{20} +0.67^\circ$, has a sweet flavour, and is not reduced by sodium and boiling amyl alcohol. As the hydrocarbon does not contain an asymmetric carbon atom, the small rotatory power must result from the presence of an impurity.

3-Methyl- $\Delta^{4(9)}$ -menthadiene, $\text{C}_{11}\text{H}_{18}$, is a colourless, mobile oil, b. p.

$71-73^{\circ}/10$ mm., D^{20}_D 0.8402, n^{20}_D 1.47252, $[\alpha]^{20}_D$ -81.41°, -96.89°, is not reduced by sodium and amyl alcohol, and when oxidised by potassium permanganate yields acetone and an acid, which crystallises in white prisms, m. p. 153—154°. A mixture of this acid with adipic acid, m. p. 149—150°, had m. p. 120—127°. G. Y.

Isomerisation Phenomena during the Preparation of Cadinene. NICOLAUS JEPESCHKIN (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 698—699).—In order to investigate the genetic relations of the sesquiterpenes obtained from oleum cadinum, the author has studied the actions of hydrogen chloride and acetic acid on cadinene.

Cadinene dihydrochloride decomposes on heating, yielding cadinene exhibiting the following constants: b. p. 148—149°/20 mm., D^{20}_D 0.9172, n^{20}_D 1.5107, $[\alpha]^{20}_D$ -111.28°. But on prolonged heating in a sealed tube at 180—200°, cadinene dihydrochloride undergoes isomeric change into an unstable chloride, which yields a sesquiterpene having b. p. 145—148°/20 mm., D^{20}_D 0.9061, n^{20}_D 1.5041, and $[\alpha]^{20}_D$ -2.80°; this sesquiterpene is probably identical with the one obtained by Schindelmeyer (this vol., i, 353), and is isomeric with the one previously obtained by the author (this vol., i, 278) by the action of hydriodic acid on the sesquiterpene having $[\alpha]^{20}_D$ -14.12°.

When cadinene is heated with acetic acid at 180—200°, its rotation falls from -111.28° to -8°; the products formed have not been investigated.

The purest cadinene prepared by the author was obtained by the action of sodium ethoxide on the dihydrochloride, and has the following constants: b. p. 149°/20 mm. and 271—272° at ordinary pressure, D^{20}_D 0.9183, n^{20}_D 1.5073, and $[\alpha]^{20}_D$ -110.96°. T. H. P.

Constituents of Essential Oils. Elemicin, a High-boiling Constituent of Elemi Oil, and the Displacement of Alkyloxy-groups in the Benzene Nucleus by Hydrogen. FRIEDRICH W. SEMMLER (*Ber.*, 1908, 41, 1768—1775).—The author has investigated the composition of the fraction of crude elemi oil which has the highest boiling point. The specimen studied had D^{20}_D 1.031, n^{20}_D 1.5188, and on analysis gave figures pointing to the presence of a benzene derivative, accompanied by small amounts of a sesquiterpene alcohol. A fraction, b. p. 150—156°/10 mm., obtained on further distillation over sodium, had D^{20}_D 1.036, n^{20}_D 1.54193, was slightly levorotatory, and is considered to consist of elemicin, $\text{CHMe}:\text{CH}\cdot\text{C}\begin{smallmatrix} \text{CH}\cdot\text{C}(\text{OMe}) \\ \text{CH}\cdot\text{C}(\text{OMe}) \end{smallmatrix}\text{C}\cdot\text{OMe}$ (I). The

propenyl group may be formed by intramolecular change of an allyl group during the distillation over sodium. When reduced with sodium and alcohol, elemicin yields an optically inactive product, $\text{C}_{12}\text{H}_{18}\text{O}_2$ (II), b. p. 125.5°/10 mm., D^{20}_D 0.994, n^{20}_D 1.51200. Oxidation of elemicin by means of potassium permanganate in acetone solution leads to the formation of 3:4:5-trimethoxybenzoic acid. When treated with sodium and alcohol, this acid is reduced to *m*-methoxybenzoic acid. *o*-Methoxybenzoic, veratric, asaronic, and myristic acids, on the other hand, are not reduced by sodium and alcohol. G. Y.

Constituents of Essential Oils. Elemicin and *iso*Elemicin. FRIEDRICH W. SEMMLER (*Ber.*, 1908, 41, 1918—1921. Compare preceding abstract).—When treated with ozone in moist benzene solution, elemicin, which has not been distilled over sodium, yields trimethyl elemicin, which has not been distilled over sodium, yields trimethylhomogallaldehyde and trimethylhomogallie acid, but after distillation homogallaldehyde and trimethylhomogallie acid. Elemicin therefore contains an ethylene linking in the β -position in the side-chain, and, when distilled over sodium, undergoes isomerisation into *isoelemicin*, which has the ethylene linking in the $\alpha\beta$ -position.

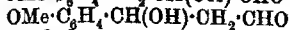
Trimethylhomogallaldehyde, $C_{11}H_{15}O_4$, b. p. $162-165^\circ/10$ mm., forms a semicarbazone, m. p. 188° . Trimethylhomogallie acid, $C_{11}H_{14}O_5$, m. p. $119-120^\circ$, forms a methyl ester, b. p. $172-182^\circ/10$ mm., D^{20}_D 1.153.

Trimethylgallaldehyde (3:4:5-trimethoxybenzaldehyde), $C_{10}H_{12}O_4$, m. p. 75° , b. p. $163-165^\circ/10$ mm., forms a semicarbazone, $C_{11}H_{14}O_5N_2$, m. p. 218° , and the aldoxime, $C_{10}H_{11}O_3.NOH$, m. p. $82-84^\circ$, b. p. $198-200^\circ/10$ mm. When heated with acetic anhydride, the aldoxime is converted into 3:4:5-trimethoxybenzonitrile, $C_{10}H_{11}O_3N$, m. p. 93° , b. p. $180-185^\circ/10$ mm., which on hydrolysis yields trimethoxybenzoic acid. G. Y.

Ethereal Oils, Material for the Investigation of. ROURE-BERTRAND FILS (*Chem. Zentr.*, 1908, i, 464—465; from *Wiss. indust. Ber. Roure-Bertrand Fils*, 1907, [2], 8, 15—32).—Oil from Sandal Wood.—A yield of 3.8% oil, $[\alpha]_D + 47.07^\circ$, D^{20}_D 0.9799, found to contain 0.4% ester and 44.1% alcohol calculated as linalyl acetate and linalool. Oil from Linaloe Seeds.— $[\alpha]_D + 1.5^\circ$, after acetylation $[\alpha]_D - 3.2^\circ$, D^{20}_D 0.8883, saponification number 29.2, 10.2% ester calculated as linalyl acetate, saponification number after acetylation 164.5, 51.6% alcohol calculated as linalool. Oil of Sage from Grasse.—Two samples examined, $[\alpha]_D + 6.13^\circ$, $+ 6.45^\circ$, D^{20}_D 0.915, 0.916, saponification number 13.4, after acetylation 53.7. Climate and soil are stated to influence the physical and chemical constants of this oil. Oil from *Tetranthera polyantha* var. *citrata*.—(1) From the bark: $[\alpha]_D + 20.5^\circ$, after acetylation $+ 8.77^\circ$, D^{20}_D 0.8673, saponification number 252.3; contains 8% citral, 10% citronellal, 56.5% alcohols, and 2.4% esters. (2) From the leaves: $[\alpha]_D - 15.5^\circ$, after acetylation $- 4.3^\circ$, D^{20}_D 0.9013, saponification number after acetylation 104.7; contains 6% citral, 21.2% cineol, and 31.3% alcohols. (3) From the fruit: $[\alpha]_D + 12.7^\circ$, after acetylation $+ 10.2^\circ$, D^{20}_D 0.8872, saponification number after acetylation 172.5; contains 64% citral, 19.4% alcohols, and 2% esters. Oil from *Magnolia Kobus* D. C.— $[\alpha]_D - 1.33^\circ$, D^{20}_D 0.9432; contains about 15% citral and a small quantity of anethole and estragole (1). J. V. E.

Lævorotatory Component of Tarragon Oil. MAURICE DAUFRENEZ and FLAMENT (*Bull. Soc. chim.*, 1908, [iv], 3, 656—658. Compare this vol., i, 19).—The lævorotation of the higher boiling fractions of tarragon oil is shown to be due to the presence of an unstable aldehyde, which on heating loses water and resinifies. It has already been suggested that the source of the *p*-methoxycinnam-

aldehyde noted as a constituent of the oil may be an aldehyde-alcohol of the constitution $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CHO}$ or



(*Bull. Soc. chim.*, 1908, [iv], 3, 330).

T. A. H.

Congo-Copal and (White) Benguela-Copal. A. ENGEL (*Arch. Pharm.*, 1908, 246, 293—305).—The portion of Congo-copal soluble in ether yields to sodium carbonate *Congocopalic acid*, $\text{C}_{19}\text{H}_{30}\text{O}_2$, m. p. 115—118° (48—50%), *α-Congocopaloresen* (5—6%), and an ethereal oil (3—4%); the residue, soluble in alcohol and ether, yields *Congocopalolic acid*, $\text{C}_{25}\text{H}_{34}\text{O}_2$, m. p. 108—110° (22%), and *β-Congocopaloresen*, m. p. 175—178° (12%); impurities and ash, 4—5%. For Benguela-copal the corresponding results are: *Bengucopalic acid*, $\text{C}_{19}\text{H}_{30}\text{O}_2$, m. p. 134—136° (13—45%), *α-Bengucopaloresen* (4—5%), ethereal oil (3—4%), *Bengucopalolic acid*, $\text{C}_{21}\text{H}_{32}\text{O}_2$, m. p. 114—116° (a lower homologue of *Congocopalolic acid*), 22%, and *β-Bengucopaloresen*, $\text{C}_{22}\text{H}_{36}\text{O}_2$, m. p. 192—196°. All these substances are amorphous.

G. B.

Fagopyrum-Rutin. A. WUNDERLICH (*Arch. Pharm.*, 1908, 246, 241—256).—The glucoside from the flowers of buckwheat (*Polygonum fagopyrum*) is identical with rutin from rue and with violaquercitrin (viola-rutin); it has the formula $\text{C}_{27}\text{H}_{36}\text{O}_{16} \cdot 3\text{H}_2\text{O}$.

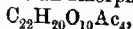
The quercetin trimethyl ether of Waliaschko (*Äbstr.*, 1904, i, 760), m. p. 154°, is hydrolysed by alcoholic potassium hydroxide to methylphloroglucinol and veratric acid; since hydroxyl groups in the ortho-position to the carbonyl groups are not directly methylated, this substance must be 1-hydroxy-3:3':4'-trimethoxyflavanol. It yields on acetylation *diacetylquercetin trimethyl ether*, $\text{C}_{15}\text{H}_5\text{O}_7 \cdot \text{Me}_3\text{Ac}_3$, m. p. 170—171°. The yellow substance, m. p. 240°, obtained by Waliaschko (*loc. cit.*) is *quercetin methyl ether*, $\text{C}_{15}\text{H}_5\text{O}_7 \cdot \text{Me}$, and yields *tetra-acetyl-quercetin methyl ether*, $\text{C}_{15}\text{H}_5\text{O}_7 \cdot \text{MeAc}_4$, m. p. 156—157°; this methyl ether differs from the three known quercetin monomethyl ethers. Acetyl-rutin, m. p. 114—116°, amorphous, probably contains nine acetyl groups, and would then have the composition $\text{C}_{27}\text{H}_{21}\text{O}_{16}\text{Ac}_9$.

G. B.

Rhamnosides from Capparis spinosa and Globularia alypum. A. WUNDERLICH (*Arch. Pharm.*, 1908, 246, 256—259).—The above rhamnosides are identical with rutin (compare preceding abstract).

G. B.

Sakuranin, a new Glucoside from the Bark of Prunus Pseudo-Cerasus var. Sieboldi. Y. ASAHINA (*Arch. Pharm.*, 1908, 246, 259—272).—*Sakuranin*, $\text{C}_{23}\text{H}_{24}\text{O}_{10} \cdot 4\text{H}_2\text{O}$, is extracted by water from the bark of the Japanese cherry tree, and is obtained crystalline after precipitation of impurities by basic aluminium acetate solution. Crystallised from alcohol or ethyl acetate, it forms white needles, m. p. 210—212°, has a bitter taste and dissolves in alkalis with an intense yellow colour; it yields an amorphous *acetyl* derivative,



and a crystalline *benzoyl* derivative, $\text{C}_{22}\text{H}_{20}\text{O}_{10} \cdot \text{Bz}_4$, m. p. 227°. On hydrolysis, sakuranin yields equal molecules of dextrose and *sakuranetin*, $\text{C}_{16}\text{H}_{14}\text{O}_2$, crystals from ether or benzene, m. p. 150°. The latter

substance contains one methoxyl group, absorbs bromine, and, when fused with potassium hydroxide, yields phloroglucinol, acetic and *p*-hydroxybenzoic acids. Sakuranin is physiologically inert, and does not produce glycosuria (like phloridzin).
G. B.

New Reduction Products of Artemisin. PASQUALE BERTOLO (*Gazzetta*, 1908, 38, i, 554—559).—According to Rimini (*Soc. Chim. Roma*, Jan. 12, 1908), santonin and artemisin contain the same fundamental nucleus, the latter compound containing a hydroxyl group in place of a hydrogen atom of the former: santonin, $\cdot\text{CO}\cdot\text{CH}\cdot\text{CMe}$, artemisin, $\cdot\text{CO}\cdot\text{C}(\text{OH})\cdot\text{CMe}$. The author points out that artemisin cannot contain a hydroxyl group, since it does not yield an acetyl or benzoyl derivative, and, on reduction with zinc dust and acetic acid, forms a dehydropinarone, artemisone (compare Bertolo and Ranfaldi, *Abstr.*, 1905, i, 897). The formation of the latter compound, which may be regarded as an oxysantonone, indicates the presence in the molecule of a carbonyl group adjacent to a methylene group,
 $\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CMe}$.

The action of various reducing agents on artemisin has been studied, the results being as follows.

Reduction of artemisin with hydriodic acid and red phosphorus gives a good yield of a compound, m. p. 98—99°, crystallising from water in shining needles and somewhat resembling artemisic acid (compare *Abstr.*, 1904, i, 177). Reduction with sodium amalgam gives an almost quantitative yield of an acid, m. p. 170°, of which the ethyl ester was prepared. Reduction by means of chromous hydroxide yields a small proportion of a substance which retains the lactonic linking and a ketonic carbonyl group, and has the same m. p., 170°, as santonin and, like the latter, turns yellow in the light and gives a violet coloration with sulphuric acid and ferric chloride; this substance is also obtained by reducing artemisin with ferrous hydroxide. Reduction of the hydrazone of artemisin with sodium amalgam gives an acid, m. p. 116°, which contains nitrogen.
T. H. P.

Nearest Acid Derivatives of the Chlorophyllins. LEON MARCHLEWSKI, (*Ber.*, 1908, 41, 1858—1860. Compare Marchlewski and Schunck, *Trans.*, 1900, 77, 1080).—Polemical. A criticism of Tsvet's recent communication (this vol., i, 440).
W. H. G.

Tetrahydropyrone Compounds. PAVEL PETRENKO-KRITSCHENKO and L. DEMENTYEFF, (*Ber.*, 1908, 41, 1696—1697).—Ethyl 2:6 diphenyltetrahydropyrone-3:5 dicarboxylate in cold alcoholic solution reacts with concentrated alcoholic potassium hydroxide to form the salt, $\text{O} \begin{array}{c} \diagup \text{CHPh} \\ \diagdown \text{CHPh} \end{array} \text{---} \text{C}(\text{CO}_2\text{Et})_2 \text{---} \text{C}\cdot\text{OK}$, whilst from the boiling solution cinnamic, benzylidenemalonic, and malonic acids have been isolated, and benzaldehyde detected by its odour.
C. S.

Oxidation Products of Aconine. HEINRICH SCHUIZE (*Arch. Pharm.*, 1908, 246, 281—292. Compare *Abstr.*, 1906, i, 599).—By the oxidation of aconine, ($\text{C}_{25}\text{H}_{41}\text{O}_3\text{N}$), with chromic acid, two substances,

$C_{24}H_{35}O_8N$ and $C_{24}H_{33}O_8N$, are formed, of which the former has basic and the latter both acid and basic properties; they appear to be an amino-alcohol and the corresponding amino-acid, and the acid has also been obtained by oxidation of the alcohol.

To the description of the base previously published, the following should be added. From analyses of the hydrochloride, the base has undoubtedly the formula $C_{24}H_{35}O_8N$, and the alternative formula $C_{24}H_{33}O_8N$, previously suggested, is now definitely excluded. The hydrochloride has $[\alpha]_D^{20} + 54.37^\circ$; the free base, m. p. $157-160^\circ$, its sulphate, and its aurichloride are all amorphous; the hydriodide, $C_{24}H_{35}O_8N \cdot HI \cdot 3H_2O$, forms fine needles, m. p. $220-230^\circ$ (decomp.). On acetylation, a crystalline tetra acetyl derivative, m. p. 233° (decomp.), is formed, and, as the substance was previously shown to contain three methoxy-groups, seven of the eight oxygen atoms are thus accounted for, and the formula of the acetyl derivative may be written $C_{20}H_{19}O_5Ac_4(OMe)_3NMe$. The aurichloride of the acetyl derivative was also analysed.

Besides having one methoxy-group less, the base, $C_{24}H_{35}O_8N$, differs from aconine in reducing acid potassium permanganate, and also in forming a methiodide. The latter forms needles from alcohol, m. p. 222° (decomp.), and has the composition $C_{25}H_{33}O_8NI$. The only product which could be isolated on further oxidation of the base, $C_{24}H_{35}O_8N$, was a minute quantity of the hydrochloride of the under-mentioned amino-acid.

The amino-acid, $C_{24}H_{33}O_8N$, is formed from aconine in larger quantity than the alcohol if much chromic acid is used. Its hydrochloride forms glassy plates and short prisms, soluble in water with acid reaction, of the composition $C_{20}H_{21}O_6(OMe)_3NMe \cdot HCl \cdot \frac{1}{2}H_2O$ (decomp. above 250°). The crystalline barium salt, $C_{48}H_{63}O_{13}N_2Ba \cdot 10H_2O$, and the crystalline hydrochloride of the amorphous methyl ester,

$C_{19}H_{20}O_4(OMe)_3(NMe) \cdot CO_2Me \cdot HCl$,
m. p. $215-220^\circ$ (decomp.), have also been analysed. G. B.

Carnine and Inosic Acid. FRANZ HAISER and FRANZ WENZEL (*Monatsh.*, 1908, 29, 157-175. Compare Nœberg and Brahm, *Abstr.*, 1907, i, 1097; Bauer, *Abstr.*, 1907, i, 1098).—Carnine, originally obtained from meat extract by Weidel (*Abstr.*, 1871, 716), is shown to be an approximately equal molecular mixture of hypoxanthine and a new substance, inosine, so named because it is evidently closely related to, and is probably derived from, the same parent substance as inosic acid. By slightly modifying the method of Weidel (*loc. cit.*), the authors have obtained about 5-6 grams each of carnine and inosic acid from one pound of fresh meat extract.

Inosine, $C_{10}H_{12}O_5N_4$, may be separated from carnine by repeated extraction with small quantities of water, in which it is fairly soluble, or by treating carnine with acetic anhydride and sodium acetate, when it is obtained in the form of an acetate, $C_{10}H_9O_2N_4(OAc)_3$ or $C_{30}H_{10}O_3N_8(OAc)_9$, crystallising in glistening, silky needles or rhomboidal plates, m. p. 236° (decomp.). Inosine crystallises in slender, silky needles, m. p. 215° (decomp.); $[\alpha]_D^{20} - 49.2^\circ$; $[M]_D^{20} - 131.8^\circ$ (in water); 100 c.c. of the saturated solution in water at 20° contains

1.615 grams of inosine; the *silver* salt, obtained as a gelatinous precipitate, is soluble in ammonia. Inosine is hydrolysed when boiled with dilute sulphuric acid, yielding hypoxanthine and a *pentose*, the *osazone* of which, $C_8H_8O_3(N \cdot NHPh)_2$, crystallises in microscopic, pale yellow needles, m. p. 163° (decomp.).

Hypoxanthine aurichloride, $C_8H_4ON_4HAuCl_4$, crystallises in glistening, prismatic needles. W. H. G.

True Tannates of Quinine. II. PIETRO BIGINELLI (*Gazzetta*, 1908, 38, i, 559—582. Compare Abstr., 1907, i, 955).—The author has prepared a number of true and false tannates of quinine and has studied their behaviour towards various reagents, the results obtained differing in some instances from those of Muraro (this vol., i, 451).

Hydrochloric acid acts on true tannates of quinine in the same way as dilute sulphuric acid, first displacing the tannic acid from its combination with quinine and then, as quinine salt, combining with the displaced tannic acid. Both the undissolved and dissolved portions represent pseudo-tannates, the nature of the former being independent of that of the true tannate employed; the dissolved false tannate, being, however, derived from quinine dihydrochloride, varies with the particular true tannate used.

In the action of tannic acid on quinine, several tannates of quinine are obtained, certain of them being formed in preference to the others according to the proportions of the components and the experimental conditions.

All the pseudo-tannates of quinine described in the various pharmacopœias are prepared from quinine sulphate or disulphate. They may be distinguished from the true tannates of quinine by the following methods: (1) 0.2—0.3 gram of the tannate is treated with a little moderately concentrated hydrochloric acid for a few minutes, after which 2—3 c.c. of water are added, and in a short time the acid decanted away. The yellow residue is treated with about 20 c.c. of water, with which it is shaken three or four times at intervals. If the residue dissolves completely, the original tannate is a true tannate of quinine, whilst, if there remains an undissolved residue, the compound examined is a pseudo-tannate derived from quinine sulphate or disulphate; (2) 0.2—0.3 gram of the tannate is treated with 2—3 c.c. of concentrated nitric acid, which is afterwards removed by heating on a water-bath. After cooling, the residue is treated with 20—30 c.c. of water and filtered, the filtrate being heated to 70° with a few drops of barium nitrate solution and then left. The gradual deposition of barium sulphate indicates a pseudo-tannate.

The following represent the compositions of the true tannates of quinine described by the author, the percentages of quinine present being indicated in brackets: $5C_{20}H_{21}O_2N_2 \cdot 5C_{14}H_{10}O_6$ (50.15); $4C_{20}H_{21}O_2N_2 \cdot 5C_{14}H_{10}O_6$ (41.59); $2C_{20}H_{21}O_2N_2 \cdot 3C_{14}H_{10}O_6$ (40.14); $2C_{20}H_{21}O_2N_2 \cdot 4C_{14}H_{10}O_6$ (33.47); $2C_{20}H_{21}O_2N_2 \cdot 5C_{14}H_{10}O_6$ (28.70); $2C_{20}H_{21}O_2N_2 \cdot 6C_{14}H_{10}O_6$ (25.11); $2C_{20}H_{21}O_2N_2 \cdot 7C_{14}H_{10}O_6$ (23.32); T. H. F.

Cytisine. EMIL MAASS (*Ber.*, 1908, 41, 1635—1637).—The conclusion that one of the nitrogen atoms of cytisine is secondary, the other being tertiary, is supported by the preparation of *cytisine cytisingldithiocarbamate*, $C_{11}H_{13}ON_2 \cdot CS \cdot SH, NH : C_{11}H_{13}ON$, from carbon disulphide; it forms a white powder, m. p. 197—198°, decomp. 200°. Hydrochloric acid regenerates cytisine and carbon disulphide; copper acetate, mercuric chloride, and silver nitrate give reddish-brown, white crystalline, and white, flocculent precipitates respectively.

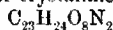
Benzoylcytisine, $C_{18}H_{18}O_2N_2$, prepared by the Schotten-Baumann method, is difficult to purify; it forms prisms, m. p. 116°.

W. R.

Sparteine. XII. CHARLES MOUREU and AMAND VALEUR (*Bull. Soc. chim.*, 1908, [iv], 3, 674—678. Compare Scholtz, Abstr., 1906, i, 379).—Further results of work on the α and α' -sparteine methiodides (Abstr., 1905, i, 608, 609, 659) are given. The two isomerides may be separated by crystallisation from alcohol. When pure, the α' -methiodide has $[\alpha]_D -47.2^\circ$, solubility in water 8% at 15°, and furnishes a hydriodide having $[\alpha]_D -40.32^\circ$ in water, which, when heated, yields the same sparteine hydriodide as is obtained from the hydriodide of the α -isomeride (*loc. cit.*). Sparteine dihydriodide, $C_{15}H_{28}N_2 \cdot 2HI \cdot H_2O$, $[\alpha]_D -15.91^\circ$, does not react with methyl iodide even when heated with it in a closed tube at 140—150°.

T. A. H.

Strychnos Alkaloids. I. New Method of Oxidising Brucine and Strychnine. HERMANN LEUCHS (*Ber.*, 1908, 41, 1711—1720).—When brucine and strychnine are oxidised with permanganate in acetone solution, 25% yields of crystalline acids, brucinonic acid,



and strychninonic acid, $C_{21}H_{20}O_8N_2$, are formed respectively. These acids contain four atoms of oxygen more and two atoms of hydrogen less than the corresponding alkaloids, and it is suggested that they are formed by the rupture of an ethylene linking with the production of two carboxyl groups and at the same time the oxidation of a secondary alcoholic to a carbonyl group. The acids are thus regarded as ketonic dibasic acids. In addition to these acids, small amounts of dihydrobrucinonic acid, $C_{23}H_{18}O_8N_2$, and dihydrostrychninonic acid, $C_{21}H_{22}O_8N_2$, are also formed; these are probably the secondary alcohols corresponding with the ketonic acid.

Brucinonic acid crystallises from water in colourless prisms containing H_2O , and has m. p. 178—183° (corr.), but when anhydrous sinters at 225° and melts at 266° (corr., decomp.); $[\alpha]_D -48.5^\circ$. It dissolves readily in sodium carbonate solution, and behaves as a monobasic acid towards phenolphthalein or litmus. Solutions of its sodium salt yield precipitates with cupric sulphate, ferric chloride, silver nitrate, and lead acetate. The *monoethyl ester*, $C_{26}H_{28}O_8N_2$, obtained by the Fischer-Speyer method, crystallises from absolute alcohol in colourless prisms, m. p. 132°, or from glacial acetic acid in prisms, m. p. 161—163°.

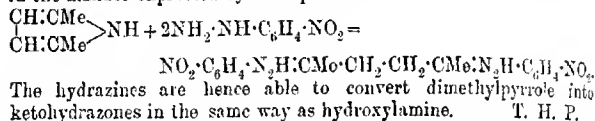
Dihydrobrucinonic acid crystallises from hot glacial acetic acid in

minute needles; it is levorotatory in concentrated solution, but dextro-rotatory in more dilute solution.

Strychninonic acid crystallises from hot water in colourless prisms containing $2\text{H}_2\text{O}$. When anhydrous, it melts and decomposes at $265\text{--}267^\circ$ (corr.), and has $[\alpha]_D^{20} - 43.3^\circ$. *Dihydrostrychninonic acid* crystallises in rectangular plates, decomposes at about 315° (corr.), and has $[\alpha]_D^{20} + 4.3^\circ$ in 3.5% solution. The acids are not poisonous.

J. J. S.

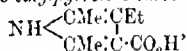
A Transformation of Dimethylpyrrole. ANGELO ANGELI and GUERRIERO MARCHETTI (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 485—486. Compare this vol., i, 207).—The interaction of ethyl formate and 2:5-dimethylpyrrole yields a mixture which, with *p*-nitrophenylhydrazine, gives a small quantity of a hydrazone, which is probably acetylacetone-*p*-nitrophenylhydrazone. This compound, which is also obtained when 2:5-dimethylpyrrole is treated with *p*-nitrophenylhydrazine, is formed by the opening of the pyrrole ring in the manner expressed by the equation:



T. H. P.

Synthesis of Ethyl 2:5-Dimethyl-3-ethylpyrrole-4-carboxylate. GEORG KORSCHEN (*Bull. Soc. chim.*, 1908, [iv], 3, 593—595. Compare Abstr., 1905, i, 373).—A continuation of work on the synthesis of similar esters by Hantzsch's method (Abstr., 1899, i, 1153).

Ethyl 2:5-dimethyl-3-ethylpyrrole-4-carboxylate,



m. p. $74\text{--}75^\circ$, could not be prepared by treating a mixture of ethyl acetoacetate and methyl α -chloropropyl ketone with ammonia, but a yield of about 27% of the theoretical was eventually obtained by the replacement of ethyl acetoacetate by ethyl β -aminocrotonate. The ester is difficult to purify by recrystallisation, and recourse was had to treating the crude product with a boiling solution of potassium hydroxide in methyl alcohol, which attacks the associated impurities, but has no action on the pyrrole ester. The latter was finally obtained in colourless, brilliant, bulky crystals from dilute methyl alcohol.

T. A. H.

Condensation of Acetonedicarboxylic Esters with Aldehydes under the Influence of Ammonia and Amines. III. PAVEL PETRENKO-KRITSCHENKO and W. PETROFF (*Ber.*, 1908, 41, 1692—1695. Compare Abstr., 1906, i, 452; 1907, i, 708).—The substances described previously as the nitrosoamines of the esters of 2:6-diphenylpiperidone-3:5-dicarboxylic acid and its *N*-methyl homologue are in reality the nitrites, since the bases are liberated by ammonium hydroxide in the cold.

The piperidone structure of the condensation products of ethyl acetonedicarboxylate with aldehydes has been proved by oxidising ethyl 2:6-diphenylpiperidone-3:5-dicarboxylate with chromic and acetic acids, whereby a substance, $C_{23}H_{21}O_5N$, m. p. 195° , is obtained, which receives the constitution $NH \langle \begin{smallmatrix} CPh:C(CO_2Et) \\ CPh:C(CO_2Et) \end{smallmatrix} \rangle CO$, because it does not give a coloration with ferric chloride, and is hydrolysed without fission by concentrated boiling alcoholic potassium hydroxide, yielding the acid, $C_{19}H_{13}O_5N$, m. p. 258° (decomp.).

The piperidone bases in benzene solution form salts with mineral acids which are insoluble in water. When, however, an alcoholic solution of the base is treated with a mineral acid, excepting nitric, the salts are not precipitated by the addition of water; from the solutions, ammonium hydroxide and platinum tetrachloride precipitate the unchanged bases and the platinumchlorides respectively. The nitrites and nitrates, however, do not exist in the soluble forms, and are precipitated by the addition of these acids to the solutions of the salts. The nitrate of ethyl diphenylpiperidonedicarboxylate, $C_{23}H_{23}O_5N.HNO_3$, m. p. $154-157^\circ$, has been prepared in this way.

C. S.

Decomposition of 3 Methyl 2-Hydrogen Quinolinat. ALFRED KIRPAL (*Monatsh.*, 1908, 29, 227-234. Compare Abstr., 1907, i, 722).—It has been proved that the compound obtained as a by-product in the preparation of 2-methyl 3-hydrogen quinolinat by the action of methyl alcohol on the anhydride of the acid is 3-methyl 2-hydrogen quinolinat (Abstr., 1906, i, 697). The ammonium quinolinamat derived from the ester is converted by the action of alkaline hypobromite into a compound which must be 3-aminopicolinic acid, since, when heated above its melting point, it liberates carbon dioxide, yielding 3-aminopyridine (compare Pollak, Abstr., 1895, i, 391).

The quinolinamat is also converted through the diazo-compound into a substance which must be 3-hydroxypicolinic acid, for it yields 3-hydroxypyridine on distillation.

3-Aminopicolinic acid, $2NH_3 \cdot C_5H_3N \cdot CO_2H, H_2O$, crystallises in faintly coloured plates, m. p. 210° (decomp.).

3-Hydroxypicolinic acid, $OH \cdot C_5H_3N \cdot CO_2H$, crystallises in colourless prisms or small, triangular plates, m. p. 215° .

W. H. G.

Nitration of Quinoline and its Mononitro-derivatives. II. ADOLF KAUFMANN and HANS HÜSSY (*Ber.*, 1908, 41, 1735-1742. Compare Abstr., 1906, i, 984).—Quinoline when nitrated yields a mixture of equal amounts of 5- and 8-nitroquinolines. The 5-nitro-derivative on further nitration yields 5:7-dinitro-, and the 8-mononitro- yields 6:8-dinitro-quinoline (Claus and Hartmann's 5:8-dinitro-quinoline). 6-Nitroquinoline yields a mixture of 5:6- and 6:8-dinitroquinolines, and 7-nitroquinoline yields a mixture of the 5:7- and 7:8-dinitro-compounds.

The 6:7-dinitroquinoline cannot be obtained by direct nitration or by synthesis.

6:8-Dinitroquinoline is obtained free from the isomeric 5:6-compound when 6-nitroquinoline is added gradually to a mixture of sulphur trioxide and concentrated nitric acid, and the temperature allowed to rise gradually to 100° while the mixture is stirred. The constitution of the dinitroquinolines has been established by their syntheses from substituted anilines by Skraup's method, using either arsenic or picric acid as oxidising agent.

The melting points are 5:7, 180°; 5:6, 185°; 7:8, 221—223°. The 5:7-dinitro-compound dissolves in aqueous sodium hydroxide, yielding a red solution, whereas the 7:8-compound yields a yellow solution. The dinitro-compounds do not combine directly with methyl iodide; the 5:6-derivative, however, combines with methyl sulphate, and from this sulphate a *methiodide*, $C_9H_5O_4N_2 \cdot MeI$, can be obtained by double decomposition. It crystallises from water in brilliant dark red plates, and decomposes at 125—126°.

J. J. S.

Fixation of Aromatic Amines on Vinyl Ketones. 4-Alkylquinolines. EDMOND E. BLAISE and M. MAIRE (*Bull. Soc. chim.*, 1908, [iv], 3, 658—667).—The authors have studied the condensation of aromatic amines with vinyl ketones. In absence of water, the action of aniline on the β -chloro-ketones gives rise to the formation of 4-alkylquinolines. This is a general method of synthesis, and gives pure compounds, although the yield is not very good.

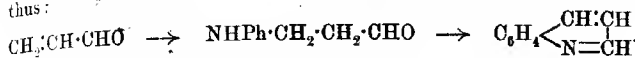
β -Anilinoethyl ethyl ketone, $NHPh \cdot C_2H_4 \cdot COEt$, is obtained by heating a mixture of aniline, water, and ethyl chloroethyl ketone on the water-bath, and crystallises from ether in plates, m. p. 55.5°. The *semicarbazone* has m. p. 130° (decomp.), and the *phenylcarbamide*, m. p. 76—77°. β -Anilinoethyl propyl ketone, $NHPh \cdot C_2H_4 \cdot COPr$, prepared from chloroethyl propyl ketone, separates from alcohol in pale yellow leaflets, m. p. 60°. The *phenylcarbamide* has m. p. 107—108°. β -Methylanilinoethyl ethyl ketone, $NPhMe \cdot C_2H_4 \cdot COEt$, has b. p. 164°/15 mm.; the *semicarbazone* has m. p. 163°, and the *picrate*, m. p. 110°. β -2-Carboxyanilinoethyl ethyl ketone, $CO_2H \cdot C_6H_4 \cdot NH \cdot C_2H_4 \cdot COEt$, has m. p. 106°.

4-Ethylquinoline (see following abstract) is obtained by heating on the water-bath a mixture of aniline (3 mols.), aniline hydrochloride (1 mol.), ethyl β -chloroethyl ketone (1 mol.), and an amount of absolute alcohol equal to the weight of the aniline hydrochloride. β -Anilinoethyl ethyl ketone is an intermediate product in this reaction, for it yields 4-ethylquinoline when heated with aniline hydrochloride.

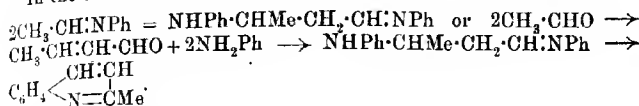
J. C. C.

4-Alkylquinolines. Mechanism of the Reactions of Skraup and of Doebner and Miller. EDMOND E. BLAISE and M. MAIRE (*Bull. Soc. chim.*, 1908, [iv], 3, 667—674).—In view of the light thrown on the mechanism of the formation of quinolines (see preceding abstract), the authors consider that both Skraup's reaction and that due to Doebner and Miller can be explained in the same way. Skraup's reaction is to be regarded as (1) formation of an acrolehyde; (2) fixation of a mol. of aniline on the double linking, and (3) ring

formation by elimination of water and loss of two atoms of hydrogen, thus:



In the case of Doebner and Miller's reaction, the mechanism is:

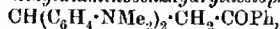


4-Ethylquinoline (preceding abstract) has b. p. 134°/9 mm. The following salts are described: *picrate*, canary-yellow needles, m. p. 193° (decomp.), *dichromate*, brown needles, m. p. 94°, *platinichloride*, orange crystals, m. p. 208° (decomp.), *aurichloride*, yellow needles, m. p. 156°, *mercurichloride*, needles, m. p. 161°, *cadmiobromide*, needles, m. p. 204°, *methiodide-di-iodide*, brown crystals, m. p. 120—121°. On oxidation with chromic acid, 4-ethylquinoline yields cinchoninic acid.

4-Propylquinoline (Koenigs, Abstr., 1899, i, 75), prepared from aniline and β -chloroethyl propyl ketone, has b. p. 159°/16 mm.; the *picrate*, m. p. 204°, the *platinichloride*, m. p. 198° (decomp.), the *mercurichloride*, m. p. 148°, the *cadmiobromide*, m. p. 148°. J. C. C.

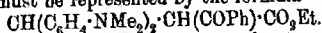
Constitution of the Compounds of Tetramethyldiaminobenzhydrol with some Methylenic Derivatives. ROBERT FOSSE (*Compt. rend.*, 1908, 146, 1039—1042. Compare Abstr., 1907, i, 414).

—The condensation of this alcohol with methylene compounds can be most simply represented thus: $\text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2\cdot\text{OH} + \text{HCHXY} = \text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2\cdot\text{CHXY} + \text{H}_2\text{O}$. But the fact that all the compounds produced, when treated with dimethylamine in the presence of acetic acid, regenerate the methylene compound and give the leuco-base of crystal-violet suggests that the combination occurs through the oxygen atom, thus: $\text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2\cdot\text{OH} + \text{HO}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et} = \text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2\cdot\text{O}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$. From the behaviour of the condensation compounds, however, the author concludes that in neutral or alkaline solution they have the constitution first suggested. Thus ethyl tetramethyldiaminobenzhydriylacetylacetate, $\text{C}_{25}\text{H}_{32}\text{O}_3\text{N}_2$, must have the constitution $\text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2\cdot\text{CH}(\text{COMe})\cdot\text{CO}_2\text{Et}$, since it forms an *oxime*, crystalline needles, m. p. 205°, and on hydrolysis loses carbon dioxide, giving a new ketone, pp *tetramethyldiaminobenzhydriylpropenone*, $\text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2\cdot\text{CH}_2\cdot\text{COMe}$, needles, m. p. 110°, which forms an *oxime*, m. p. 136—137°, a *semicarbazone*, m. p. 185° (decomp.), a *dihydrochloride*, and a *platinichloride*. As ethyl tetramethyldiaminobenzhydriylbenzoylacetate, $\text{C}_{25}\text{H}_{32}\text{O}_3\text{N}_2$, on hydrolysis loses carbon dioxide, giving *tetramethyldiaminobenzhydriylacetophenone*,



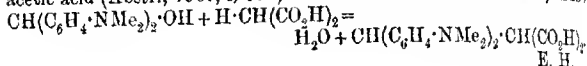
fine brilliant needles, m. p. 145°, which forms an *oxime* and a *platinichloride*, whilst, when treated with concentrated alcoholic potash, it undergoes simultaneously both "acid" and "ketone" hydrolysis, giving benzoic and tetramethyldiaminobenzhydriylacetic acids, tetra-

methyldiaminobenzhydrylaceto-phenone, carbon dioxide, and alcohol, its constitution must be represented by the formula

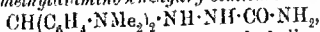


Similarly, tetramethyldiaminobenzhydrylacetylaceto-ene should be represented by $\text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2\cdot\text{CH}(\text{COMe})_2$, since alcoholic potash transforms it into potassium acetate and the substituted propanone described above. Again, alcoholic potash converts tetramethyldiaminobenzhydrylbenzoylaceto-ene into a mixture of the two mono-ketones, tetramethyldiaminobenzhydrylaceto-ene and tetramethyldiaminobenzhydrylaceto-phenone, and therefore $\text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2\cdot\text{CH}(\text{COMe})\cdot\text{COPh}$ must be the formula of the diketone.

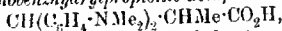
The oxide formula is inapplicable to tetramethyldiaminobenzhydrylaceto-ene and its derivatives, which must have the constitution $\text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2\cdot\text{CH}(\text{CO}_2\text{H})_2$. This acid can be prepared from the ethyl ester or it can be obtained directly. When malonic acid reacts with the hydrol, there is formed either tetramethyldiaminobenzhydrylaceto-ene (Abstr., 1907, i, 136) or the substituted malonic acid, thus:



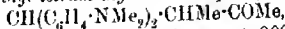
Constitution of the Methylene Derivatives of Tetramethyldiaminodiphenylmethane. Replacement of Hydroxyl in Michler's Carbinol by the Alkylmethylene Radicle. ROBERT FOSSE (*Compt. rend.*, 1908, 146, 1277—1280. Compare preceding abstract).—The author has extended his work on the condensation of tetramethyldiaminobenzhydryl. The constitution of the methylene derivatives described in the present paper is not in accord with Weil's ketonic formula (Abstr., 1894, i, 419) for the carbinol. The compounds have the constitution $(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2\text{CH}\cdot\text{CXYR}$, and give a colourless solution with cold acetic acid, which becomes intensely blue on heating. They are decomposed in acetic acid solution in presence of dimethylaniline into the methylenic constituent and the leuco-base of crystal-violet. Methyl tetramethyldiaminobenzhydrylmethylacetate, $\text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2\cdot\text{CMeAc}\cdot\text{CO}_2\text{Me}$, has m. p. 113—114°. Under the influence of semicarbazide, it yields methyl methylacetate and tetramethyldiaminobenzhydrylsemicarbazide,



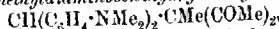
m. p. 185—187°, and when treated with alcoholic potash furnishes α -tetramethyldiaminobenzhydrylpropionic acid,



sintering at 170°, m. p. 190°, the ethyl ester of which has m. p. 103—104°, and methyl tetramethyldiaminodiphenylisopropyl ketone,



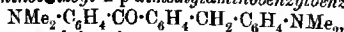
m. p. 144—145°; the semicarbazone sinters at 200°, m. p. 215—216° (decomp.). Tetramethyldiaminobenzhydrylmethylacetate,



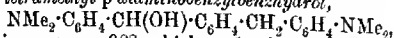
has m. p. 140—143°. With alcoholic potash, it gives methyl tetramethyldiaminodiphenylisopropyl ketone.

J. C. C.

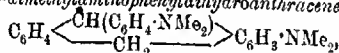
Amino-derivatives of *o*-Dibenzoylbenzene. ALFRED GUYOT and P. PIGNET (*Compt. rend.*, 1908, 146, 984—987. Compare Guyot and Catel, *Abstr.*, 1905, i, 226, 516, 540; 1906, i, 761; 1907, i, 76). —*p*-Dimethylaminobenzoyl-2-*p*-dimethylaminobenzylbenzene,



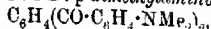
m. p. 133°, prepared by the condensation of dimethylaniline with *p*-dimethylaminobenzoyl chloride in the presence of aluminium chloride, forms pale yellow needles, and does not yield condensation products with hydrazine, phenylhydrazine, hydroxylamine, or semicarbazide; it forms a trinitro-derivative, $\text{C}_{24}\text{H}_{23}\text{O}_7\text{N}_5$, m. p. 174°, crystallising in brilliant yellow prisms; it is reduced by sodium amalgam to tetramethyl-*p*-diaminobenzylbenzhydrol,



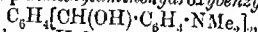
colourless prisms, m. p. 98°, which on further reduction yields 1:2-di-*p*-dimethylaminobenzylbenzene, $\text{C}_6\text{H}_4(\text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$, m. p. 90°. When tetramethyldiaminobenzylbenzhydrol is mixed with concentrated sulphuric acid, it loses H_2O and forms an anthracene derivative, 2-dimethylamino-9-*p*-dimethylaminophenyldihydroanthracene,



n. p. 168°, which on oxidation with chloranil loses H_2 and is converted into 2-dimethylamino-9-*p*-dimethylaminophenyldihydroanthracene, $\text{C}_{24}\text{H}_{21}\text{N}_2$, m. p. 184°. 1:2-Di-*p*-dimethylaminobenzylbenzene,

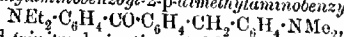


n. p. 207°, obtained as pale yellow prisms by the oxidising action of chloranil on *p*-dimethylaminobenzoyl-2-*p*-dimethylaminobenzylbenzene, yields a monophenyldiazone, $\text{C}_{26}\text{H}_{26}\text{ON}_4$, m. p. 194°, a dioxime, $\text{C}_{24}\text{H}_{22}\text{O}_2\text{N}_4$, m. p. 230°, and a phthalazine, $\text{C}_{24}\text{H}_{24}\text{N}_4$, m. p. 281°; it yields on reduction 1:2-di-*p*-dimethylaminohydroxybenzylbenzene,

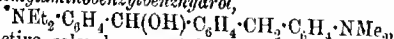


m. p. 124°, which loses H_2O by the action of phosphoryl chloride and is converted into 1:2-*p*-dimethylaminophenyl-1:2-dihydroisobenzofuran, $\text{C}_6\text{H}_4 \left\langle \begin{array}{c} \text{CH}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2) \\ \text{CH}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2) \end{array} \right\rangle \text{O}$, m. p. 145°.

The diethyl homologues of the above compounds have also been prepared: *p*-diethylaminobenzoyl-2-*p*-diethylaminobenzylbenzene,



m. p. 104°, and trinitro-derivative, $\text{C}_{25}\text{H}_{22}\text{O}_7\text{N}_5$, m. p. 125°; *p*-diethylamino-*p*-dimethylaminobenzylbenzhydrol,



highly refractive, colourless crystals, m. p. 73°; 1-*p*-diethylaminobenzyl-*p*-dimethylaminobenzylbenzene, $\text{NEt}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$

n. p. 57°; the dihydroanthracene derivative, $\text{C}_{25}\text{H}_{23}\text{N}_2$, m. p. 113 the anthracene derivative, $\text{C}_{26}\text{H}_{25}\text{N}_2$, m. p. 132°; 1-*p*-diethylaminobenzoyl-*p*-dimethylaminobenzylbenzene, $\text{NEt}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$,

n. p. 110°, and its phthalazine, $\text{C}_{25}\text{H}_{23}\text{N}_4$, m. p. 189°, and phenyldiazone, $\text{C}_{24}\text{H}_{24}\text{ON}_4$, m. p. 170°.

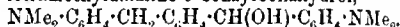
M. A. W.

Some *o*-Benzylated Dyes from Triphenylmethane. ALFRED GUYOT and P. PIGNET (*Compt. rend.*, 1908, 146, 1043—1045).—The

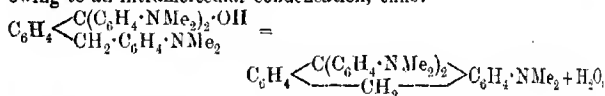
stability towards alkalis conferred on dyes of the type of malachite green by substituting groups in the ortho-position to the methane carbon atom is usually explained by a steric protection by these groups. On this hypothesis, it would be expected that groups of higher molecular weight would have a proportionally greater effect, and it has been found, in fact, that the benzyl group has a protective action of the same order as the sulphonic group when substituted in the ortho-position. The tetra-alkyldiamino-*o*-benzoylbenzylbenzenes,

$\text{C}_6\text{H}_4 \begin{cases} \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NR}_2 & (1) \\ \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NR}_2 & (2) \end{cases}$, and the tetra-alkyldiamino-*o*-benzylbenzylbenzenes, $\text{C}_6\text{H}_4 \begin{cases} \text{CH}(\text{OH}) \cdot \text{C}_6\text{H}_4 \cdot \text{NR}_2 & (1) \\ \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NR}_2 & (2) \end{cases}$ (preceding abstract), readily

condense with various amines, giving *o*-benzylated malachite-greens or their leuco-derivatives. Thus dimethylaniline in the presence of phosphoryl chlorido reacts with tetramethyldiamino-*o*-benzoylbenzylbenzene, giving *o*-dimethylaminobenzylphenyltetramethyldiaminodiphenylcarbinol, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2 \cdot \text{OH}$, which can be isolated in the form of small, reddish-brown crystals of the zincchloride, $\text{C}_{32}\text{H}_{26}\text{N}_8\text{Cl}_2\text{Zn}$. The dye also forms a double nitrate with potassium, $\text{C}_{32}\text{H}_{26}\text{O}_6\text{N}_8\text{K}$, beautiful crystals having a coppery reflex, and a similar sodium salt. The leuco-base, $\text{C}_{32}\text{H}_{28}\text{N}_8$, fine white needles, m. p. 162° , is easily obtained by reducing the dye with zinc and hydrochloric acid, or by the direct condensation of dimethylaniline with tetramethyldiamino-*o*-benzylbenzhydrol,



This dye, like all the amido-dyes derived from triphenylmethane, dissolves in concentrated sulphuric acid with an orange-red coloration; in this instance, however, the liquid is rapidly decolorised, owing to an intramolecular condensation, thus:



giving 2:13:13'-hexamethyltrianino-9:9'-diphenyldihydroanthracene, a white, crystalline powder, m. p. 175° , giving colourless solutions in dilute mineral acids.

By using diethylaniline in place of the methyl derivative, the homologue of the above dye is obtained, and can be isolated in the form of the zincchloride, $\text{C}_{34}\text{H}_{30}\text{Cl}_2\text{N}_8\text{Zn}$, and the double nitrates with sodium and potassium, $\text{C}_{34}\text{H}_{30}\text{O}_6\text{N}_8\text{Na}$ and $\text{C}_{34}\text{H}_{30}\text{O}_6\text{N}_8\text{K}$. The leuco-base, $\text{C}_{34}\text{H}_{32}\text{N}_8$, has m. m. 107° .

When *o*-dimethylaminobenzyl-diethylaminobenzoylbenzene is similarly condensed with diethylaniline, an *o*-dimethylaminobenzyl derivative in the form of a brilliant green is produced. This gives the double nitrates $\text{C}_{36}\text{H}_{41}\text{O}_6\text{N}_8\text{K}$ with potassium, and $\text{C}_{36}\text{H}_{41}\text{O}_6\text{N}_8\text{Na}$ with sodium, and a leuco-derivative, $\text{C}_{36}\text{H}_{43}\text{N}_8$, m. p. 118° . E. H.

Striking Fluorescence Phenomena in Picryl Compounds. HEINRICH LEY [in part F. MÜLLER and P. KRAFFT] (*Ber.*, 1908, 41, 1637—1644).—It has already been noted that $\alpha\beta$ -diphenyl- γ -benzyl-hydroxyamidine picrate and analogous compounds (*Abstr.*, 1901, 1,

739) are strongly fluorescent, a result in direct contradiction to the generalisation that the introduction of nitro-groups depresses the fluorescence. The same phenomenon is observed with the picryl compounds of diguanidide, guanylformamidide, and diformamidide. Ley and Muller have likewise shown that abnormally coloured and very stable salts are given by analogous amidides (Abstr., 1907, i, 730), and the fluorescence may be explained in a similar way, the supplementary valencies of the picryl radicle acting on a basic group, :NPh for example.

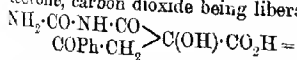
Whereas the free diphenylbenzylhydroxyamidide has only a shallow band, and picryl chloride no absorption in the ultra-violet; yet the picryl derivative has two well-defined bands, one in the greenish-violet and the other in the ultra-violet. The fluorescent spectrum has also a broad band in the visible spectrum, but no rays could be detected in the ultra-violet, a result in partial harmony with the conclusion drawn by Stark and Meyer that there is a parallelism between the absorption and fluorescent spectra (Abstr., 1907, ii, 418; compare, also, ii, 147). The results are not in harmony with Hewitt's theory (Abstr., 1900, ii, 318), but may be explained by Stark's (this vol., ii, 138) or by Collie and Bily's oscillation hypothesis (Trans., 1905, 87, 1332).

The fluorescence diminishes in the order of the following solvents: ethyl acetate, chloroform, benzene, carbon tetrachloride, acetone, carbon disulphide, amyl alcohol, ethyl alcohol, methyl alcohol.

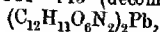
The dark orange picryl- $\alpha\beta$ -diphenyl- γ -benzylhydroxyamidide crystallises from a mixture of chloroform and light petroleum in yellow crystals, which are composed of 13 or 14 mols. of amidide and 1 mol. of solvent, m. p. 110°.

Picrylphenyldiguanide, $\text{NH}\cdot\text{C}(\text{NHPh})\cdot\text{N}[\text{C}_6\text{H}_2(\text{NO}_2)_3]\cdot\text{C}(\text{NH}_2)\cdot\text{NH}$, obtained from the hydrochloride, picryl chloride, and sodium ethoxide, forms glistening, brownish-red crystals, m. p. 205°, and has a yellowish-green fluorescence in acetone. Neither diguanide nor β -diphenyl diguanide gives fluorescent picryl derivatives, but *picryl- $\beta\delta\epsilon$ -triphenyl-guanylamidide*, $\text{NH}\cdot\text{CPh}\cdot\text{N}[\text{C}_6\text{H}_2(\text{NO}_2)_3]\cdot\text{C}(\text{NHPh})\cdot\text{NPh}$, red needles, m. p. 182°, gives intense yellow, fluorescent solutions. W. R.

Phenacyl-dialuric Acid, tartronuric Acid, and isohydantoic Acid. OTTO KÜHLING (*Ber.*, 1908, 41, 1658—1664).—The compound obtained in the attempt to benzoylate phenacyldialuric acid by the Schotten-Baumann method, and previously described as phenacyl-alanturic acid (Abstr., 1905, i, 944), is now shown to be phenacyl-isohydantoic acid, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{COPh}$, since it is obtained by boiling solutions of phenacyltartronuric acid in water or acetone, carbon dioxide being liberated, thus:



Phenacyltartronuric acid is obtained by treating phenacyldialuric acid with dilute aqueous sodium carbonate solution; it crystallises in microscopic needles, m. p. 144—145° (decomp.). The lead salt,



needle-shaped prisms, silver salt, $C_{12}H_{11}O_4N_2Ag$, a thick, gelatinous precipitate, and sodium salt, $C_{12}H_{10}O_4N_2Na_2$, a white, flocculent precipitate, were prepared and analysed.

Phenacylisohydantoic acid crystallises in concentrically grouped leaflets, m. p. $161-162^\circ$ (decomp.). W. H. G.

Some Methods of Preparation of Triazans. GUIDO GOLD-SCHMIEDT (*Ber.*, 1908, 41, 1862-1864).—Polemical. The compound obtained by Michaelis (this vol., i, 471) from *as*-phenylbenzylhydrazine by various methods of preparation and supposed to be diphenyldibenzyltriazan is undoubtedly phenylbenzylbenzylidenetriazone, a compound always present in old specimens of *as*-phenylbenzylhydrazine (compare Ofner, Abstr., 1904, i, 818; Milrath, following abstract).

The compound described by Michaelis (*loc. cit.*) as triphenylbenzyltriazan is probably diphenylbenzylidenetriazone. W. H. G.

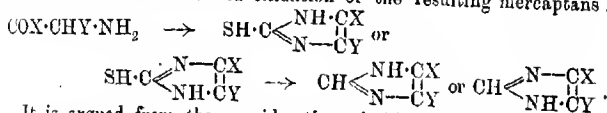
Conditions of Formation of Phenylsemicarbazide and of Acetylphenylhydrazine. HUGO MILRATH (*Monatsh.*, 1908, 29, 337-350).—The author has repeated Jaffé's work on the production of phenylsemicarbazide from carbamido, phenylhydrazine, and acetic acid (Abstr., 1897, ii, 575), and finds that either acetylphenylhydrazine or a mixture of this with phenylsemicarbazide is obtained in this reaction. For the exclusive formation of the latter, the transformation of carbamido into ammonium cyanate is necessary, as is also a high temperature, a long period of heating, and an increased concentration of carbamido. Acetylphenylhydrazine is largely formed by warming equal molecular quantities of phenylhydrazine and 7% acetic acid on the water-bath. Dog's and cat's urine, rich in carbamido, furnish phenylsemicarbazido only when warmed for four to five hours with phenylhydrazine and acetic acid; when normal human urine is used, the mixture must be warmed for at least five hours. J. C. C.

Condensation of Gallocyanin Dyes with Amino-compounds. EUGÈNE GRANDMOUGIN and ERNST BODMER (*J. pr. Chem.*, 1908, [ii], 77, 498-510. Compare Abstr., 1907, i, 355).—It was shown previously (this vol., i, 289) that pruneanilide and correinanilide are formed by condensation of prune and correin with aniline. Details are now given of the preparation of similar condensation products of prune with *m*- and *p*-aminobenzoic acids, *o*-, *m*-, and *p*-nitroanilines, methylaniline, *p*-phenylenediamine, and benzidine. The substance obtained by condensation of prune with sulphanic acid is not identical with the product of the sulphonation of pruneanilide. *Prune sulphate*, $C_{16}H_{14}O_5N_2 \cdot H_2SO_4$, olive leaflets, and *piecate*, $C_{16}H_{14}O_5N_2 \cdot C_6H_3O_7N_3$, green leaflets, were analysed. Coelestin-blue B (correin RR) forms a green, crystalline *piecate*, $C_{17}H_{17}O_4N_3 \cdot C_6H_3O_7N_3$. The condensation of the base with *o*-, *m*-, and *p*-aminobenzoic acids, *m*- and *p*-nitroanilines, and diethyl-*p*-phenylenediamine is described. G. Y.

Hydantoin and the Isomerism of the Methylhydantoins. CARL D. HARRIES (*Annalen*, 1908, 361, 69—72).—The *iso-ε*-methylhydantoin described by Harries and Weiss (Abstr., 1903, i, 738) has now been found to be a mixture of *ε*-methylhydantoin and smaller amounts of another substance, which has not been completely separated; on repeated recrystallisation, fractions, m. p. 147—156° and m. p. 178°, were obtained.

When heated with alcoholic ammonia at 100°, ethyl hydantoate yields hydantoin, and not aminoacetamide as previously stated (*loc. cit.*). G. Y.

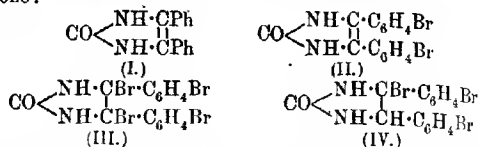
Tautomerism in the Iminazole Series. SIEGMUND GABRIEL (*Ber.*, 1908, 41, 1926—1928).—The virtual tautomerism of the benziminazoles having been demonstrated by Fischer, the present work was undertaken to determine if in the case of the simple monocyclic iminazoles, isomerides, such as $\text{CH} \begin{smallmatrix} \text{NH} \cdot \text{CX} \\ \text{N} - \text{CY} \end{smallmatrix}$ and $\text{CH} \begin{smallmatrix} \text{N} - \text{CX} \\ \text{NH} \cdot \text{CY} \end{smallmatrix}$, are capable of separate existence, or if only one tautomeric substance is obtainable. It was shown previously (Abstr., 1893, i, 734) that iminazoles are formed by the action of thiocyanic acid on α -amino-ketones and oxidation of the resulting mercaptans:



It is argued from the consideration of this scheme that, if the iminazoles be not tautomeric, the iminazole prepared in this manner from α -aminopropiophenone, $\text{COPh} \cdot \text{CHMe} \cdot \text{NH}_2$, must be isomeric with that derived from α -amino- α -phenylacetone, $\text{COMe} \cdot \text{CHPh} \cdot \text{NH}_2$. It is found, however, that the two amino-ketones yield the same 4-phenyl-5-methyl- or 5-phenyl-4-methyl-iminazolyl mercaptan (Behr-Bregowski, Abstr., 1897, i, 458), which forms white leaflets, becoming rose-red at about 260°, sinter about 280°, m. p. 298—299°. Phenyl-methyliminazole, formed by the oxidation of the mercaptan with nitric acid, crystallises in white leaflets, m. p. 185°, forming a brownish-violet liquid. G. Y.

Bromination of Diphenylglyoxalane. I. HEINRICH BILTZ and CHAIM RIMPEL (*Ber.*, 1908, 41, 1754—1760).—When boiled with bromine in chloroform solution and treated with water, diphenylglyoxalane (I) yields 4:5-di-*p*-bromodiphenylglyoxalane (II) together with small amounts of di-*p*-bromobenzil and di-*p*-bromodiphenylacetylenediureine. The main reaction is found to take place in several stages, the first, which is complete at the ordinary temperature, leading to the formation of 4:5-di-*p*-bromodiphenylglyoxalane dibromide (III). At higher temperatures, this is converted by the hydrogen bromide liberated during the first stage into 4-bromo-2-keto-4:5-di-*p*-bromodiphenyltetrahydroglyoxalane (IV), which when treated with

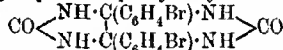
water loses hydrogen bromide and forms 4:5-di-*p*-bromodiphenylglyoxalane:



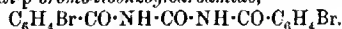
The intermediate substances (III) and (IV) are formed also by the action of bromine and hydrogen bromide respectively on di-*p*-bromodiphenylglyoxalane.

Di-*p*-bromodiphenylglyoxalane, $\text{C}_{16}\text{H}_{10}\text{ON}_2\text{Br}_2$, crystallises from alcohol in colourless, rectangular plates, m. p. 328° , or from glacial acetic acid in microscopic needles containing $\text{C}_2\text{H}_4\text{O}_2$, is soluble in alcoholic alkalis, and is oxidised by liquid nitrogen dioxide or concentrated nitric acid, forming di-*p*-bromobenzil, $\text{C}_6\text{H}_4\text{Br} \cdot \text{CO} \cdot \text{CO} \cdot \text{C}_6\text{H}_4\text{Br}$ (see following abstract). In the same manner, diphenylglyoxalane yields benzil when treated with nitric acid or sodium nitrite in concentrated sulphuric acid solution. The diacetyl derivative, $\text{C}_{18}\text{H}_{12}\text{ON}_2\text{Br}_2\text{Ac}_2$, crystallises in rhombic plates, m. p. $192-193^\circ$, and is readily hydrolysed by alcoholic potassium hydroxide.

Di-*p*-bromodiphenylglyoxalane dibromide, $\text{C}_{16}\text{H}_{10}\text{ON}_2\text{Br}_4$, prepared by the action of bromine on diphenylglyoxalane or di-*p*-bromodiphenylglyoxalane in glacial acetic acid, chloroform, or benzene solution, crystallises in yellow, rectangular plates and needles, reacts with carbamide, forming di-*p*-bromodiphenylacetylenediureine,

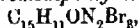


(see following abstract), and when heated with water is converted into the glycol, $\text{CO} < \begin{array}{c} \text{NH} \cdot \text{C}(\text{C}_6\text{H}_4\text{Br}) \cdot \text{OH} \\ \text{NH} \cdot \text{C}(\text{C}_6\text{H}_4\text{Br}) \cdot \text{OH} \end{array} >$ which decomposes into di-*p*-bromobenzil and carbamide, the latter reacting with unchanged dibromide to form di-*p*-bromodiphenylacetylenediureine. A similar decomposition takes place when the dibromide is treated with sodium hydroxide, but is accompanied by another reaction, leading to the formation of *s*-di-*p*-bromotibenzoylcarbamide,



When recrystallised from glacial acetic acid, di-*p*-bromodiphenylglyoxalane dibromide decomposes to the extent of about 33%, forming di-*p*-bromodiphenylglyoxalane, di-*p*-bromobenzil, and di-*p*-bromodiphenylacetylenediureine. In analogy to this, the same three end products are obtained, in varying proportions, when phenylglyoxalane is treated with bromine in concentrated sulphuric acid and the resulting dibromide precipitated by addition of ice, or when diphenylglyoxalane is allowed to remain in contact with bromine and water.

4-Bromo-2-keto-4:5-di-*p*-bromodiphenyltetrahydroglyoxaline,



prepared by the action of bromine and hydrogen bromide on di-*p*-bromodiphenylglyoxalane in chloroform solution, crystallises in light brown prisms, decomp. about 240° , and loses hydrogen bromide,

forming di-*p*-bromodiphenylglyoxalane when boiled with xylene, or more slowly when boiled with alcohol, glacial acetic acid, or ether.

4. *Bromo-2 keto-4:5-diphenyltetrahydroglyoxaline*, $\text{CO} \begin{smallmatrix} \text{NH} \cdot \text{CBrPh} \\ \text{NH} \cdot \text{CHPh} \end{smallmatrix}$,

prepared by saturating a chloroform solution of diphenylglyoxalane with hydrogen bromide, crystallises in colourless prisms, and loses hydrogen bromide when treated with water.

s-Di-*p*-bromodibenzoylcarbamide, obtained on adding chromic anhydride to 4:5-di-*p*-bromodiphenylglyoxalane in boiling glacial acetic acid solution, or by oxidising the dibromo-compound with sodium hypobromite, crystallises in needles, m. p. 250° (decomp.) when quickly, or 245—247° (decomp.) when slowly, heated, forming *p*-bromobenzonitrile, is readily soluble in nitrobenzene, and on hydrolysis with alcoholic alkalis yields *p*-bromobenzoic acid.

When reduced with sodium and alcohol, di-*p*-bromodiphenylglyoxalane yields diphenyldihydroglyoxalane, m. p. 292—293°.

G. Y.

Bromination of Diphenylglyoxalane. II. HEINRICH BILTZ (*Ber.*, 1908, 41, 1761—1767. Compare preceding abstract).—The action of bromine on diphenylglyoxalane in boiling glacial acetic acid solution leads to the formation of di-*p*-bromobenzil, di-*p*-bromodiphenylacetylenediureine, and 5:5-di-*p*-bromodiphenylhydantoin (this vol., i, 462).

Di-*p*-bromobenzil, $\text{C}_{11}\text{H}_8\text{O}_2\text{Br}_2$, crystallises from benzene in flat needles, m. p. 228—229°, gives colour reactions with boiling alcoholic and aqueous alcoholic alkalis, and with alcoholic potassium hydroxide at the ordinary temperature forms a yellow solution which on acidification yields a slowly solidifying oil. Oxidation of di-*p*-bromobenzil with chromic anhydride in glacial acetic acid solution leads to the formation of *p*-bromobenzoic acid.

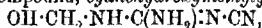
Di-*p*-bromodiphenylacetylenediureine, $\text{C}_{16}\text{H}_{12}\text{O}_2\text{N}_4\text{Br}_2$, is formed by heating di-*p*-bromobenzil with carbamide, or by the action of bromine and carbamide on di-*p*-bromophenylglyoxalane, diphenylglyoxalane, or benzoin, in glacial acetic acid solution at the ordinary temperature. It crystallises in colourless threads or leaflets, decomp. about 360°, does not form an acetyl derivative (compare Biltz, this vol., i, 62), is stable towards concentrated sulphuric acid, sodium nitrite in concentrated sulphuric or glacial acetic acid solution, and bromine, and is only slightly attacked by aqueous or alcoholic potassium hydroxide, but is decomposed by fuming nitric acid.

Di-*p*-bromodiphenylglyoxalane forms small amounts of di-*p*-bromobenzil when heated with concentrated hydrochloric acid at 160—170°, but remains unchanged when boiled with hydrogen bromide in glacial acetic acid solution; when boiled with bromine, acetic acid, and water, on the other hand, it is rapidly decomposed, forming di-*p*-bromobenzil together with small amounts of di-*p*-bromodiphenylacetylenediureine and di-*p*-bromodiphenylhydantoin.

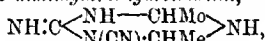
G. Y.

Dicyanodiamide. FRANZ POHL (*J. pr. Chem.*, 1908, [ii], 77, 533—548).—Although the object of numerous investigations, the constitution of dicyanodiamide has not hitherto been established with

certainty. Baumann (this Journ., 1873, 1025; 1874, 376) ascribed to dicyanodiamide the formula $\text{NH}_2\text{C} \begin{smallmatrix} \text{NH} \\ \text{NH} \end{smallmatrix} \text{C:NH}$, whilst Klason (Abstr., 1886, 324) and Hofmann (Abstr., 1886, 41) preferred the form $\text{NH}_2\text{C} \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} \text{C:NH}_2$. Bamberger, on the other hand, considered the substance to be a cyanoguanidine, $\text{NH}_2\text{C}(\text{NH}_2)\cdot\text{NH}\cdot\text{CN}$ (Abstr., 1883, 907, 1090); in discussing this constitution, it is necessary to take into consideration the tautomeric form $\text{CN}\cdot\text{N}:\text{C}(\text{NH}_2)_2$. The present author has found that, on treatment with sodium hypobromite solution, dicyanodiamide readily loses half its nitrogen, a behaviour which points to the presence of two amino-groups. When heated with 2 mols. of benzoic anhydride, dicyanodiamide forms benzoic acid, benzonitrile, carbon dioxide, dibenzoylcarbamide, and *dibenzoyldicyanodiamide*, $\text{CN}\cdot\text{N}:\text{C}(\text{NHBz})_2$. With formaldehyde, dicyanodiamide forms an additive compound, *cyanohydroxymethylguanidine*,



but with acetaldehyde and ammonia a compound, which is probably 1-imino-6-cyano-3:5-dimethylhexahydrotriazine,



is formed, whilst with the sodio- β -keto-esters, dicyanodiamide forms 2-cyanoimino-4-alkyluracils, $\text{CN}\cdot\text{N}:\text{C} \begin{smallmatrix} \text{NH}\cdot\text{Calk} \\ \text{NH} \text{---} \text{CO} \end{smallmatrix} \text{CH}$, or 2-cyano-

amino-6-keto-4-alkylpyrimidines, $\text{CN}\cdot\text{NH}\cdot\text{C} \begin{smallmatrix} \text{N}\text{---}\text{Calk} \\ \text{N}:\text{C}(\text{OH}) \end{smallmatrix} \text{CH}$. It is considered that these reactions show that dicyanodiamide reacts in both of the tautomeric forms of cyanoguanidine.

Dibenzoyldicyanodiamide, $\text{C}_{16}\text{H}_{12}\text{O}_2\text{N}_4$, crystallises in needles, m. p. 225° (compare Gerlich, this Journ., 1876, ii, 196), is readily soluble in cold dilute alkalis, and when heated with hydrochloric acid under pressure yields benzoic acid.

If dicyanodiamide and benzoic anhydride are heated together in molecular proportions, the product contains benzonitrile, benzoic acid, and a substance, $\text{C}_9\text{H}_8\text{O}_2\text{N}_2$, white needles, m. p. $162\text{--}163^\circ$, but not dibenzoyldicyanodiamide.

Cyanohydroxymethylguanidine, $\text{C}_2\text{H}_6\text{ON}_4$, is obtained as a white, crystalline powder, m. p. 118° , yields formaldehyde and dicyanodiamide when heated with water, and forms unstable compounds with silver and mercuric salts and with platinum tetrachloride in hydrochloric acid solution.

1-imino-6-cyano-3:5-dimethylhexahydrotriazine, $\text{C}_6\text{H}_{11}\text{N}_3$, crystallises in white needles, m. p. 190° , and is readily decomposed, forming ammonia, acetaldehyde, and dicyanodiamide when boiled with water, or more rapidly with dilute alkalis, or when heated with dilute hydrochloric acid at 40° for thirty minutes. The *picrate*, $\text{C}_{12}\text{H}_{10}\text{O}_8\text{N}_6$, was analysed. The *nitroso*-derivative, $\text{C}_6\text{H}_{10}\text{ON}_6$, forms yellow needles, m. p. 156° . The triazino reacts with anilino hydrochloride, forming ethylideneaniline, or with phenylhydrazine hydrochloride, forming phenylethylidenehydrazine.

2-Cyanoamino-6-hydroxy-4-methylpyrimidine, $\text{C}_6\text{H}_8\text{ON}_4$, prepared

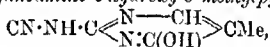
from dicyanodiamide and ethyl acetoacetate, separates from acetic acid in crystals, which become yellow at 240° , decomp. $280-285^{\circ}$. The sodium salt, $C_6H_5ON_4Na \cdot H_2O$, loses H_2O at $180-190^{\circ}$, decomp. 290° , and in aqueous solution gives characteristic precipitates with metallic salts. The silver salt, $C_6H_5ON_4Ag$, was analysed. When boiled with hydrochloric acid, the cyanoamino-compound is converted into 2-carbamido-6-hydroxy-4-methylpyrimidine, $NH_2 \cdot CO \cdot NH \cdot C \begin{smallmatrix} N-CMe \\ N:C(OH) \end{smallmatrix} CH$, which is obtained as a white, flocculent substance, sinters at 229° , m. p. $262-264^{\circ}$ becoming yellow. When heated with concentrated hydrochloric acid at 120° , the cyanoamino-compound is converted into iminomethyluracil.

2-Cyanoamino-6-hydroxy-4-phenylpyrimidine, $C_{11}H_8ON_4$, prepared from dicyanodiamide and ethyl benzoacetate, crystallises in needles, which sinter at 230° , but do not melt. 2-Carbamido-6-hydroxy-4-phenylpyrimidine, $C_{11}H_{10}O_2N_4$, is a white, amorphous powder, m. p. 234° .

2-Cyanoamino-6-hydroxy-4:5-dimethylpyrimidine, $C_7H_8ON_4$, prepared from dicyanodiamide and ethyl methylacetoacetate, crystallises from boiling alcohol in leaflets, m. p. 280° (decomp.), yields iminodimethyluracil when heated with concentrated hydrochloric acid, and when boiled with dilute hydrochloric acid is converted into 2-carbamido-6-hydroxy-4:5-dimethylpyrimidine, m. p. 269° (decomp.).

2-Cyanoamino-6-hydroxy-4-methyl-5-ethylpyrimidine, prepared from ethyl ethylacetoacetate, is obtained as a crystalline powder, m. p. 257° (decomp.); the corresponding 2-carbamido-compound forms needles, m. p. 235° .

The action of dicyanodiamide on ethyl sodioformylpropionate leads to the formation of 2-cyanoamino-6-hydroxy-5-methylpyrimidine,



which crystallises from hot water in needles, becomes yellow, but does not melt, at 293° , when heated with fuming hydrochloric acid at 120° is hydrolysed to carbon dioxide, ammonia, formic acid, and propionic acid, and when boiled with dilute hydrochloric acid yields 2-carbamido-6-hydroxy-5-methylpyrimidine, crystallising in needles, m. p. 245° . G. Y.

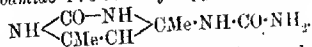
Condensation of β -Diketones with Carbamide. T. DE HAAN (*Rec. trav. chim.*, 1908, 27, 162-191. Compare Evans, *Abstr.*, 1893, i, 129; 1894, i, 111).—The compound obtained by Evans on condensing carbamide with acetylacetone crystallises with $2H_2O$ in monoclinic prisms. These are colourless when freshly prepared, but by warming in aqueous solution or on exposure to light are transformed without change of crystalline form into a yellow modification. The colourless compound is probably 4:6-dimethyl-2-pyrimidone, $CH \begin{smallmatrix} CMe=N \\ CMe-NH \end{smallmatrix} CO$, whilst the yellow modification may possess the

constitution originally ascribed to it by Evans, $CH_2 \begin{smallmatrix} CMe:N \\ CMe:N \end{smallmatrix} CO$. The potassium salt is colourless, and when treated with carbon dioxide

yields the colourless substance. The *nitrate* decomposes explosively at 245°. When acetylacetone is mixed with excess of carbamide in

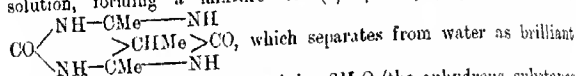
aqueous solution, $\beta\delta$ -*pentanedione*, $\text{CO} \begin{array}{c} \text{NH} \cdot \text{CMe} \cdot \text{NH} \\ > \text{CH}_2 \\ \text{NH} \cdot \text{CMe} \cdot \text{NH} \end{array} \text{CO}$, is

formed together with the diuriminoacetylacetone described by Combes (compare Abstr., 1893, i, 454). The former compound crystallises from water in lustrous plates containing 4H₂O. The anhydrous substance has m. p. 290°. Cold nitric acid converts it into a *dinitrate*, but, on warming, this is decomposed into carbamide and 2-oxy-1:6-di-methylpyrimidine. The colourless modification of Combes' compound is probably 6-carbamido-4:6-dimethyl-2-pyrimidone,



A yellow form can also be obtained, and this is regarded as a derivative of the coloured variety of 4:6-dimethyl-2-pyrimidone.

Methylacetylacetone and carbamide readily condense in aqueous solution, forming a mixture of (1) γ -methyl- $\beta\delta$ -*pentanedione*,

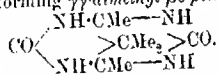


white, monoclinic crystals containing 2H₂O (the anhydrous substance darkens without melting at 316°), and (2) *carbamidobis-1:5:6-trimethyl-2-pyrimidone*, $\text{CO} \begin{array}{c} \text{NH} \cdot \text{CMe} \cdot \text{NH} \\ > \text{CMe} \cdot \text{CMe} \\ \text{NH} \cdot \text{CMe} \cdot \text{NH} \end{array} \text{CO}$. This compound, distinguished from the foregoing diureide by its solubility in alcohol, forms white needles, m. p. 203–210° with effervescence. It separates with 2H₂O from aqueous solution.

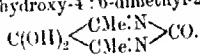
A solution of either of the two preceding compounds in nitric acid evolves carbon dioxide and nitrous oxide, and deposits the yellow unstable 4:5:6-trimethyl-2-pyrimidone *nitrate*, C₇H₁₀N₂O₂HNO₂.

The free base has the constitution $\text{CMe} \begin{array}{c} \text{CMe} = \text{N} \\ \text{CMe} \cdot \text{NH} \end{array} \text{CO}$, and, when obtained by decomposing its *potassium* salt with carbon dioxide, forms colourless needles, which separate from water with 1½H₂O.

Dimethylacetylacetone and carbamide condense when heated together at 140–160°, forming $\gamma\gamma$ -dimethyl- $\beta\delta$ -*pentanedione*,



This separates from water in colourless crystals, m. p. 270°, which contain 2H₂O. Nitric acid converts it into a substance, m. p. 266°. This is probably 5:5-dihydroxy-4:6-dimethyl-2-pyrimidone,

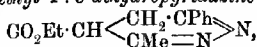


W. O. W.

Action of Hydrazine on Ethyl Phenacylacetacetate. CARL BÜLOW AND HANS FILCHER (*Ber.*, 1908, 41, 1886–1889).—Paal and Kühn (this vol., i, 57) have studied the action of hydrazine on ethyl phenacylbenzoylacetate, and the present authors now describe experi-

ments with ethyl phenacylacetoacetate, which gives rise to a similar condensation product.

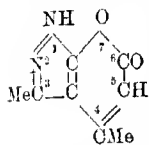
Ethyl 6-phenyl-3-methyl-4 : 5-dihydropyridazine-4-carboxylate,
(VII, C₁₇H₁₇N₂O₂)



obtained by adding hydrazine hydrate to ethyl phenacylacetate below 0°, crystallises from light petroleum in aggregates of yellow needles, m. p. 90–91°. It is not attacked by nitrous acid.

J. C. C.

3:4-Dimethyl-1:2-pyrazo-6:7-pyrone (Lactone of 5-Hydroxy-3-methylpyrazole-4-isopropylencarboxylic Acid). CARL BÉLOW and FRITZ SCHAUB (*Ber.*, 1908, 41, 1945—1947).—The sub-

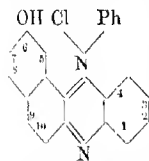


stance $C_8H_8O_2N_2$, m. p. 246–247°, which has been obtained in various ways (Knorr and Rosengarten, Abstr., 1894, i, 546; Wolff, Abstr., 1905, i, 839; Bülow and Lobeck, Abstr., 1907, i, 301), has been shown to have the annexed constitution by Stollé (Abstr., 1905, i, 838) and Wolff (*loc. cit.* this vol., i, 291).

The formation of the lactone from ethyl oxalylbishydrazonacetate at 187° (Hüllow and Lobeck, *loc. cit.*), and from ethyl acetatebenzoylhydrazonate at 175°, leads the authors to the general statement that the action of heat under suitable conditions on ethyl acetateacylhydrazones results in the formation of a diacylhydrazine and 3:4-dimethyl-1:2-pyrazo-6:7-pyroue. C. S.

C. S.

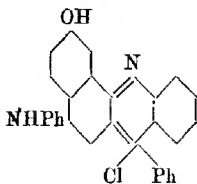
Azonium Compounds and Azines from 7-Hydroxy- β -naphthaquinone. FRIEDRICH KEHRMANN and R. BRUNEL (*Ber.*, 1908, 41, 1832-1837).—Azonium compounds containing a hydroxyl group in the meta- or para-position to the ammonium group are often converted into inner salts of a phenol-betaine character when the free bases are liberated from their salts. Thus the meta-series give *aposafranones*, *rosindones*, and *iserosindones*, and the para-series the *prasindones*.



The authors have now examined the behaviour of similar compounds containing a hydroxyl group in a different position, and find that in the case of 6-hydroxyphenylisnaphthaphenazonium chloride, annexed formula, the free base is a true ammonium base and does not form inner salts. 6-Hydroxyphenylisnaphthaphenazonium chloride, formed by condensing *o*-phenylenediamine and 7-hydroxy-

oxy- β -naphthaquinone, is obtained in black, shining leaflets. The *platinichloride* is brownish-violet. The *base* is formed by shaking the hydrochloride with silver hydroxide, but could not be isolated from the green solution. The *acetyl* derivative of the chloride is orange-red, and gives a *nitrate*, $C_{21}H_{17}O_2N_2 \cdot NO_3 \cdot H_2O$, brownish-red needles, a *platinichloride*, scarlet, crystalline powder, and a *dichromate*, long needles. By treating 6-hydroxyphenylisonaphthalphenazonium chloride with aniline, 3-anilino-6-hydroxyphenylisonaphthalphenazonium

chloride, dark blue crystals with a coppery lustre, is obtained. The fact of this substance having a blue colour was crucial in deciding on the constitution of the parent substance, for from analogy the anilino-derivative of the isomeric 9-hydroxy-naphthaphenazonium chloride, annexed formula, should be red. A small amount of this substance was contained in the mother liquor from the condensation, and was found to give a violet-red derivative with aniline.

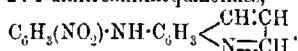


9-Hydroxynaphthaphenazonium chloride, steel-blue crystals, gives a platinumchloride. The free base is bluish-green, and could only be obtained in solution.

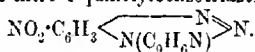
9-Hydroxynaphthaphenazine, $\text{HO} \cdot \text{C}_{10}\text{H}_5 \llbracket \text{N} \text{---} \text{N} \rrbracket \text{C}_6\text{H}_4$, obtained from *o*-phenylenediamine hydrochloride and 7-hydroxy- β -naphthaquinone, crystallises from alcohol in yellow leaflets, m. p. 235°; the hydrochloride forms golden crystals.

J. C. C.

Condensation Products of Chlorodinitrobenzene and Aminoquinolines. WILHELM MEIGEN, H. GARBS, W. MERKELBACH, and G. WICHERN (*J. pr. Chem.*, 1908, [ii], 77, 472—488).—1-Chloro-2:4-dinitrobenzene reacts with 6- and 7-aminoquinolines in boiling alcoholic solution, or with 5- and 8-aminoquinolines when fused, forming the corresponding 2:4-dinitroanilinoquinolines,



These, on reduction with ammonium sulphide, yield 1-nitro-2-aminoanilinoquinolines, $\text{NH}_2 \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{N}$, which are converted by nitrous acid into 5-nitro-1-quinolybenzotriazoles,



Reduction of the dinitro-compounds with stannous chloride and hydrochloric acid leads to the formation of 2:4-diaminoanilinoquinolines, $\text{C}_6\text{H}_3(\text{NH}_2)_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{N}$.

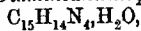
8-*op*-Dinitroanilinoquinoline crystallises in orange needles, m. p. 266°; the platinumchloride, $(\text{C}_{15}\text{H}_{10}\text{O}_3\text{N}_4)_2 \cdot \text{H}_2\text{PtCl}_6$, brownish-yellow needles, m. p. 280°. 8-*p*-Nitro-*o*-aminoanilinoquinoline, brown needles, m. p. 231°; the hydrochloride, $\text{C}_{15}\text{H}_{12}\text{O}_3\text{N}_4 \cdot \text{HCl}$, needles; the platinumchloride, $(\text{C}_{15}\text{H}_{11}\text{O}_3\text{N}_4)_2 \cdot \text{H}_2\text{PtCl}_6$, brownish-yellow crystals, m. p. 276°; the acetyl derivative, $\text{C}_{17}\text{H}_{11}\text{O}_3\text{N}_4$, yellow needles, m. p. 173°. 5-Nitro-1-*o*-quinolybenzotriazole, yellow needles, m. p. 274°, forms unstable salts. 8-*op*-Diaminoanilinoquinoline, $\text{C}_{15}\text{H}_{14}\text{N}_4 \cdot \text{H}_2\text{O}$, yellowish-green needles, m. p. 129°.

7-*op*-Dinitroanilinoquinoline forms brownish-yellow crystals, m. p. 204°. 7-*p*-Nitro-*o*-aminoanilinoquinoline, dark red needles, m. p. 215°. 5-Nitro-1-*m*-quinolybenzotriazole, m. p. 290°.

6-*op*-Dinitroanilinoquinoline crystallises in red needles, m. p. 217°; the platinumchloride forms yellow leaflets. 6-*p*-Nitro-*o*-aminoanilinoquinoline is obtained as a red powder, m. p. 215°. 5-Nitro-1-

p-quinolylbenzotriazole, white needles, m. p. 274°. 6-*op*-Diaminoanilinoquinoline, silver-grey needles, m. p. 173°, forms yellow salts.

5-*op*-Dinitroanilinoquinoline crystallises from xylene in yellowish-red needles, m. p. 211°, and forms salts which are decomposed by water; the hydrochloride and platinichloride were analysed. The methiodide, $C_{15}H_{10}O_4N_4 \cdot MeI$, formed by heating the dinitro-base with methyl iodide at 100°, crystallises in yellow needles, m. p. 164°, and yields a dark violet precipitate when treated with an alkali. 5-*p*-Nitro-*o*-aminoanilinoquinoline, brown needles, m. p. 232°; the platinichloride, brown leaflets, m. p. 276°. The acetyl derivative, yellow crystals, m. p. 215°. 5-Nitro-1-*ana*-quinolylbenzotriazole, needles, m. p. 227°. 5-*op*-Diaminoanilinoquinoline,



yellowish-green needles, m. p. 191°.

G. Y.

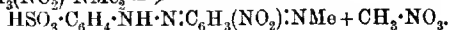
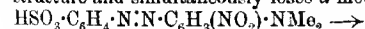
Action of *as*-Phenylbenzylhydrazine on Carbamide. HUGO MILRATH (*Ber.*, 1908, 41, 1865—1869).—Phenylbenzylsemicarbazide, obtained by heating carbamide with *as*-phenylbenzylhydrazine at 175°, or by warming equivalent quantities of the hydrazine hydrochloride and potassium cyanate in aqueous solution, has m. p. 139—140°; Michaelis (*this vol.*, i, 471) gives m. p. 103°. The diacetyl derivative, $C_{17}H_{18}O_2N_2$, crystallises in glistening needles, m. p. 128°.

Diphenyldibenzylcarbazine, $(CH_2Ph \cdot NPh \cdot NH)_2CO$, m. p. 169°, is formed when *as*-phenylbenzylhydrazine (2 mol.) is heated with carbamide (1 mol.) at 175° or with phenylbenzylsemicarbazide at a temperature not above 180°. On the contrary, a substance, $C_{14}H_{12}ON_2$, m. p. 167—168°, is obtained when *as*-phenylbenzylhydrazine and carbamide are heated together at 270°; the acetate has m. p. 81—82°; the benzoate crystallises in broad, glassy needles, m. p. 82°; a crystalline methyl derivative was also prepared.

It is probable that the compound described by Michaelis (*loc. cit.*) as diphenylbenzylaminobiuret is identical with the substance, m. p. 167—168°.

W. H. G.

Action of Dilute Nitric Acid on Helianthin. JOHN J. FOX (*Ber.*, 1908, 41, 1989—1991).—When methyl-orange is mixed with dilute nitric acid at the ordinary temperature, the dye is decomposed with formation of 2:4-dinitromethylaniline, a methyl group being eliminated. If the mixture is kept cold, the presence of a diazo-compound can also be detected. The author considers that a mononitro-helianthin may be first formed, which then assumes the quinonoid structure and simultaneously loses a methyl group, thus:



The product is then decomposed with formation of dinitromethylaniline and diazobenzenesulphonic acid.

J. C. C.

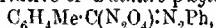
Aminoazo-compounds. JOHN T. HEWITT (*Ber.*, 1908, 41, 1986—1988).—A claim for priority. The theory of the constitution of the two forms of aminoazobenzenesulphonic acids recently put forward by Hantzsch (*this vol.*, i, 469) had already been advanced by

the author (this vol., ii, 269). The decomposition of helianthin by dilute nitric acid (Fox, preceding abstract) can only be explained on the assumption of the quinonoid formula $\text{O} \begin{array}{l} \text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} \\ \text{SO}_2 - \text{C}_6\text{H}_4 \cdot \text{NH} \end{array}$ for the free acid.

Benzeneazo-2:6-dibromoaniline has m. p. 168° (corr.), and not 191° (Hantzsch and Hilscher, this vol., i, 485). J. C. C.

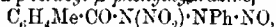
Action of Diazo-salts on Primary Dinitrohydrocarbons. GIACOMO PONZIO and G. CHARRIER (*Gazzetta*, 1908, 38, i, 526—532).—The reaction previously described (this vol., i, 482) for ω -dinitrotoluene is extended to ω -dinitro-*p*-xylene and *p*-methoxytoluene. In these cases, too, the diazobenzene derivatives, $\text{CR}(\text{N}_2\text{O}_4) \cdot \text{N}_2\text{Ph}$, readily undergo transformation into the isomeric α -nitro- β -nitroso- α -acyl- β -phenylhydrazines, $\text{R} \cdot \text{CO} \cdot \text{N}(\text{NO}_2) \cdot \text{NPh} \cdot \text{NO}$, and benzeneazodinitrohydrocarbons, $\text{N}_2\text{Ph} \cdot \text{CR}(\text{NO}_2)_2$.

The diazobenzene derivative of ω -dinitro-*p*-xylene,



m. p. 72° (decomp.), has a golden-yellow colour, dissolves in concentrated sulphuric acid, giving a green coloration, changes slowly into the isomeric red azo-compound, and gives off nitrogen when heated with alcohol.

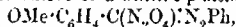
α -Nitro- β -nitroso- α -*p*-toluoyl- β -phenylhydrazine,



prepared by dissolving the diazobenzene derivative of ω -dinitro-*p*-xylene in anhydrous benzene, separates from the latter in unstable, white laminae, m. p. $97-98^\circ$ (decomp.), gives a brown coloration with concentrated sulphuric acid and phenol, and dissolves in cold water, giving a solution which almost immediately deposits β -nitroso- α -*p*-toluoyl- β -phenylhydrazine, $\text{C}_6\text{H}_4\text{Me} \cdot \text{CO} \cdot \text{NH} \cdot \text{NPh} \cdot \text{NO}$, in the form of faintly yellow laminae, m. p. $115-116^\circ$ (decomp.).

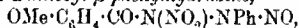
ω -Dinitro- ω -benzeneazo-*p*-xylene, $\text{NPh} \cdot \text{N} \cdot \text{C}(\text{NO}_2)_2 \cdot \text{C}_6\text{H}_4\text{Me}$, prepared from the diazobenzene derivative of ω -dinitro-*p*-xylene by heating it with alcohol or dissolving it in aqueous ether, crystallises from alcohol in orange-red prisms, m. p. $130-135^\circ$ (decomp.).

The diazobenzene derivative of ω -dinitro-*p*-methoxytoluene,



is an unstable, yellow compound, m. p. 85° (decomp.), and dissolves in concentrated sulphuric acid, giving an emerald-green solution.

α -Nitro- β -nitroso- α -anisoyl- β -phenylhydrazine,



separates rapidly from an ice-cold anhydrous benzene solution of the diazobenzene derivative of ω -dinitro-*p*-methoxytoluene in unstable, yellow laminae, m. p. $123-124^\circ$ (decomp.), and gives an emerald-green coloration with concentrated sulphuric acid and phenol; it dissolves in cold water, which rapidly transforms it into nitric acid and β -nitroso- α -anisoyl- β -phenylhydrazine (compare Bamberger and Pemsel, *Austr.*, 1903, i, 286). Boiling water converts the latter into α -anisoyl- β -phenylhydrazine, with evolution of nitrous vapours and partial resinification.

ω-Dinitro-*ω*-benzeneazo-*p*-methoxytoluene, $\text{NPh}\cdot\text{N}\cdot\text{C}(\text{NO}_2)_2\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$, is formed spontaneously from the diazobenzene derivative of *ω*-dinitro-*p*-methoxytoluene, or, more rapidly, in alcoholic, ethereal, or chloroform solution, or by shaking the benzene solution with water. It separates in blood-red, flattened needles, m. p. 141—148° (decomp.), and is moderately stable. T. H. P.

Primary Bisazo-compounds of Benzylethyl-*m*-aminophenol. CARL BÜLOW and THEODOR SPROESSER (*Ber.*, 1908, 41, 1684—1692. Compare Bülow and Wolfs, *Abstr.*, 1898, i, 308; 1899, i, 135; Bülow and Sproesser, this vol., i, 272).—The authors find that two isomeric bisazo-compounds can be obtained at will from benzylethyl-*m*-aminophenol under suitable conditions. If the substituted *m*-aminophenol in an aqueous solution slightly acidified with hydrochloric acid is treated with an equivalent quantity of a diazo-salt, $\text{RN}_2\cdot\text{X}$, the

monoazo-compound, $\text{RN}_2\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{NEt}\cdot\text{CH}_2\text{Ph}$, is obtained, which reacts in an alcoholic alkaline solution with another equivalent of a diazo-salt,

$\text{R}'\text{N}_2\cdot\text{X}$, to yield the bisazo-compound $\text{RN}_2\cdot\text{C}_6\text{H}_2(\text{OH})(\text{N}_2\text{R}')\cdot\text{NEt}\cdot\text{CH}_2\text{Ph}$.

Conversely, benzylethyl-*m*-aminophenol can be coupled in alkaline solution with an equivalent quantity of $\text{RN}_2\cdot\text{X}$, yielding

$\text{C}_6\text{H}_3(\text{OH})(\text{N}_2\text{R})\cdot\text{NEt}\cdot\text{CH}_2\text{Ph}$, which can then unite with $\text{R}'\text{N}_2\cdot\text{X}$ in acetic acid

solution, forming $\text{R}'\text{N}_2\cdot\text{C}_6\text{H}_2(\text{OH})(\text{N}_2\text{R})\cdot\text{NEt}\cdot\text{CH}_2\text{Ph}$. The following compounds

are described.

5-Benzylethylamino-2-benzeneazophenol,

$\text{N}_2\text{Ph}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{NEt}\cdot\text{CH}_2\text{Ph}$, m. p. 117°, red crystals with blue reflex. *5-Benzylethylamino-2-*p*-tolueneazophenol*, $\text{C}_{25}\text{H}_{23}\text{ON}_3$, m. p. 110°, orange-red crystals. *5-Benzylethylamino-2-*a*-naphthaleneazophenol*, $\text{C}_{25}\text{H}_{23}\text{ON}_3$, m. p. 110°, greenish-black crystals. *5-Benzylethylamino-2-benzeneazophenetole*, $\text{C}_{28}\text{H}_{25}\text{ON}_3$, m. p. 103.5°, orange-red leaflets. *5-Benzylethylamino-2-*p*-sulphobenzeneazophenol*, $\text{C}_{21}\text{H}_{21}\text{O}_4\text{N}_3\text{S}$, m. p. 230°, small, red crystals; the sodium salt contains $2\text{H}_2\text{O}$, and has m. p. 258—265° (decomp.).

5-Benzylethylamino-2:4-bisbenzeneazophenol, $\text{C}_{27}\text{H}_{25}\text{ON}_5$, m. p. 129°, greenish-black crystals with a metallic lustre, which dissolve in concentrated sulphuric acid with a green colour, becoming red on dilution. *5-Benzylethylamino-2:4-bis-*p*-tolueneazophenol*, $\text{C}_{29}\text{H}_{29}\text{ON}_5$, m. p. 154°, green prisms. *5-Benzylethylamino-2-benzeneazo-4-*p*-tolueneazophenol*, $\text{C}_{28}\text{H}_{27}\text{ON}_5$, m. p. 116°, highly refractive, green crystals, red by transmitted light. C. S.

Deaminoproteins. ZDENKO H. SKRAUP (*Biochem. Zeitsch.*, 1908, 10, 245—248. Compare Abstr., 1906, i, 913; 1907, i, 367, 739).—Deaminoproteins, obtained by the action of nitrous acid, generally contain slightly less nitrogen than the proteins from which they are derived. This diminution in the nitrogen content is apparently connected with a considerable reduction of the amount of histidine and arginine, and a complete disappearance of lysine among the products of hydrolysis. G. B.

The So-called Amidic Nitrogen of the Proteins. ZDENKO H. SKRAUP and EMIL R. VON HARDT-STREMBE (*Monatsh.*, 1908, 22, 255—262).—In the investigations hitherto recorded on the quantities of ammonia formed on the hydrolysis of proteins with hydrochloric acid, the protein has been boiled for some hours with concentrated hydrochloric acid (compare Hausmann, Abstr., 1899, i, 653; 1900, i, 317; Kutscher, Abstr., 1901, i, 107). The present communication contains the results of several determinations of the quantities of ammonia formed by boiling various proteins with both strong and dilute hydrochloric acid for from five minutes to five hours. The substances examined and the maximum amounts of ammonia they yield when boiled with hydrochloric acid are as follows: casein, 1.6%; edestin, 1.6%; serum-globulin, 1.0%; crystallised egg-albumin, 1.1%; sodium hyalinate, 0.7%, and sodium protalbinate, 1.0%. Gelatin was also examined, but, contrary to the statement of Hart (Abstr., 1901, i, 783), was found to contain no amidic nitrogen.

The maximum of amidic nitrogen is obtained by boiling with the strong acid for about five hours, but about two-thirds of the total amidic nitrogen is eliminated during the first five minutes when strong hydrochloric acid is used, and in fifteen minutes when dilute acid (1:1) is employed. The conclusion is drawn therefore that the greater part of the amidic nitrogen is eliminated during the transformation of the protein into the albumose, and that consequently the formation of the albumose from the protein is not simply a hydrolytic process, but is accompanied by the liberation of ammonia.

Ammonia is also probably evolved during the further dissociation of the albumose (compare Henderson, Abstr., 1900, i, 265). W. H. G.

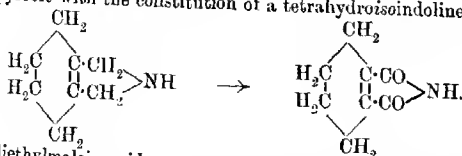
Protoplasmic Hydrolysis. ALÉXANDRE ÉTARD and ANTONY VILA (*Compt. rend.*, 1908, 146, 1155—1156).—The author discusses the conditions required for the hydrolysis of protoplasmides and the means of separating the products, pointing out important objections to the use of phosphotungstic acid. The fact is emphasised that in protoplasmic hydrolysis the true weight of the initial organic matter is never known, owing to the impossibility of completely drying it. The conclusions are drawn that the nitrogenous compounds resulting from the breaking down of protoplasmides are produced in very small quantities, that the high yields proceed from calculations of nitrogen based on hypothesis and not on experience, and that precipitates of high molecular weight give an inexact idea of the true amount of organic matter that they contain. E. H.

Action of Certain Oxidising Agents on Blood Pigments.
 JOHN A. MACWILLIAM (*Bio.-Chem. J.*, 1908, 3, 155—164).—If strong solutions of chlorates are added to blood, there is beyond the phase of methemoglobin a jellying effect. The jelly is firm, and its formation is accelerated by acidification or by warmth (30—40°), and retarded by alkalis. The red colour in time gives place to a deep green as seen by reflected light, although thin slices appear brownish-red by transmitted light. The green colour gradually changes to yellow. Sometimes the jelly contracts, squeezing out a clear fluid rich in protein, but free from iron. If the blood is diluted beyond a certain point, jellying fails, and a coloured precipitate is formed when a chlorate is added; this rapidly becomes green if acid is added. Bromates produce similar effects, but iodates produce a red precipitate with different properties. Chlorates and bromates produce the same effects with hemoglobin solutions, but not with stromata, serum, plasma, or egg-albumin. Solutions of hæmatin fail to give the results also. The altered hemoglobin is very insoluble; it, however, dissolves in alkali, dries to a dark powder, and microscopically polygonal flakes are seen. It shows no absorption bands. The product is probably due to oxidation, and is not a halogen compound.

The substance retains all the iron of the hemoglobin in very firm combination. It is digestible by peptic or tryptic enzymes, but there is no formation of hæmatin, on prolonged digestion, the iron is gradually liberated. It is suggested that chlorates and bromates may be useful in distinguishing hemoglobin from other pigments, and as fixing agents for hemoglobin in microscopical work. W. D. H.

Hæmatin. WILLIAM KÜSTER [with K. FUCHS] (*Zeitsch. physiol. Chem.*, 1908, 55, 505—556. Compare this vol., i, 303).—Further experiments were carried out on the reduction of the synthesised anhydrides of the methylethylmaleic and methylpropylmaleic acids to the corresponding succinic acids. The operations were carried out in acid solutions by zinc dust. In both cases the fumaroid form was obtained in the largest quantity (that is, 4 grams of the fumaroid form and 0.25 gram of the maleoid form). The two forms were separated from one another by means of their calcium salts.

As hemopyrrole, on oxidation, yields an imide of a dibasic acid, in order to determine its constitution, synthetical imides were prepared. In addition to the imides of methylethylmaleic and methylpropylmaleic acids, there were also prepared diethylmaleimide and the imide of Δ^1 -cyclohexene-1:2-dicarboxylic acid, which could be derived from a hemopyrrole with the constitution of a tetrahydroisindoline, thus:



The diethylmaleic acid was prepared from citraconic acid, which reacts with its anhydride presumably according to the following

equation: $C_5H_8O_4 + C_2H_4O_3 = C_8H_{10}O_3 + 2CO_2$. The imide prepared from this acid was an oil, boiling at 138—140°. Neither this nor the imide of Δ^1 -cyclohexene-1:2-dicarboxylic acid was identical with the oxidation product of h mopyrrole. The latter was obtained from Δ^1 -cyclohexene-1:2-dicarboxylic acid by first heating it above its melting point (240°), and then heating the anhydride so formed with alcoholic ammonia, also by the distillation of the substance obtained by treating the anhydride with ammonia in alcoholic and ethereal solutions; the latter substance thus prepared was amorphous, and had a composition corresponding with the formula $C_8H_{11}O_3N_2$. The anhydrides of Δ^2 -cyclohexene-1:2-dicarboxylic acid, *trans*- Δ^4 -cyclohexene-1:2-dicarboxylic acid, and *cis*- Δ^4 -cyclohexene-1:2-dicarboxylic acid were also prepared by the Baeyer methods; from these, the corresponding imides were obtained, which do not agree in properties with the oxidation product of h mopyrrole. These properties are indicated in the following table:

	Anhydride.	Imide.
	m. p.	
Phthalic acid	128°	233°
Δ^1 -cyclohexene-1:2-dicarboxylic acid	73—74	169—170
Δ^2 -cyclohexene-1:2-dicarboxylic acid	78—79	172—173
<i>cis</i> - Δ^4 -cyclohexene-1:2-dicarboxylic acid	59—60	?
<i>trans</i> - Δ^4 -cyclohexene-1:2-dicarboxylic acid	140	232—233

Evidence is given as to the existence of two h mopyrroles, obtainable by the reduction of h matin with hydriodic acid, one, an acid substance, which can be extracted from acid solutions with ether, and the other, a basic substance. An account is given of the attempts to prepare pure derivatives, and also of some oxidation experiments. A preliminary account of some oxidation experiments carried out with the non-volatile by-products in the h mopyrrole preparation is also given, by means of which h matinic acid was obtained. S. B. S.

A New Method of Tanning. LOUIS MEUNIER and ALPHONSE SEYEWETZ (*Compt. rend.*, 1908, 146, 987—989).—Hides are not greatly changed by quinol in the absence of oxygen, but, when oxygen and alkali are present, the fibre gradually becomes pink, then violet, and finally brown, and acquires perfect resistance to boiling water. The tanning depends on the formation of benzoquinone, and is also brought about by a solution of the latter substance; during the tanning process, the benzoquinone is again partly reduced to quinol. The explanation is sought in a reaction between benzoquinone and the amino-groups of the protein, similar to that between aniline and benzoquinone, which results in a condensation of aniline with part of the benzoquinone, and in the reduction of the rest of the benzoquinone to quinol. G. B.

Nucleic Acids. XIII. PHOEBUS A. LEVENE and JOHN A. MANDEL (*Biochem. Zeitsch.*, 1908, 10, 215—220. Compare Abstr., 1907, i, 266).—A method is described of obtaining pure guanine from the cleavage products of nucleic acid. The cleavage is brought about

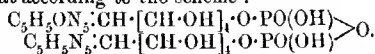
by acetic acid in the presence of lead acetate at 150°. The lead is removed by sulphuric acid, the acetic acid by distillation under reduced pressure, and the purine bases are precipitated by silver sulphate and then treated in the usual way. Some experiments are also given on the determination of the proportion between purine and pyrimidine bases, but this matter is still being investigated.

W. D. H.

The Nucleo-protein of the Liver. I. Guanylic Acid. PHÆBUS A. LEVENE and JOHN A. MANDEL (*Biochem. Zeitsch.*, 1908, 10, 221—228).—A substance corresponding with Bang's β -guanylic acid was prepared from the liver. Its reactions were not, however, absolutely identical with Bang's acid, which was made from the pancreas. In elementary composition, the figures were fairly close. From it, guanine was prepared, but no adenine; the pyrimidine bases were absent. Hexoses were absent from the molecule; a pentose was obtained, but its identification was not very certain; glycerol was not obtained.

W. D. H.

Constitution of Thymonucleic Acid. PHÆBUS A. LEVENE and JOHN A. MANDEL (*Ber.*, 1908, 41, 1905—1909).—In continuation of an investigation of the intermediate products formed by the hydrolysis of nucleic acids (Abstr., 1904, ii, 955), it has been observed that, on hydrolysis with dilute mineral acids, thymonucleic acid yields, on the one hand, products containing carbohydrate groupings and traces of phosphoric acid, but without reducing action on Fehling's solution, and, on the other, substances which do not contain purine bases, but on further hydrolysis yield phosphoric acid, levulic acid, and thymine. By hydrolysis of thymonucleic acid by 2% sulphuric acid at 150°, there has now been obtained an amorphous *barium thyminglucophosphate*, $C_{11}H_{12}O_{10}N_2P_2Ba$, which, when heated with 25% sulphuric acid at 175°, yields thymine and levulic and phosphoric acids. The composition of the thyminglucophosphoric acid is almost identical with that of hemi-nucleic acid (Schmiedeberg, Abstr., 1900, i, 267; Alsberg, Abstr., 1904, i, 791), and may be considered to be a mononucleotide. It is suggested that the nucleic acids are composed of simpler complexes, the nucleotides, each formed of phosphoric acid, a carbohydrate, and a base, these complexes uniting to form polyphosphoric acids. The bases are combined with the carbohydrates, probably in the form of glucosides, somewhat according to the scheme:



According to this view, the complex nucleic acids are constituted in the same manner as the simpler guanylic and inosic acids, but, whilst these readily yield free carbohydrates or reducing glucophosphoric acids when hydrolysed, the presence of the carbohydrate groups in the immediate products of the hydrolysis of thymonucleic acid can be detected only by the colour reactions with orcinol, or by hydrolysis to levulic acid.

G. Y.

Adsorption of Ferments. LEONOR MICHAELIS and M. EHRENREICH (*Biochem. Zeitsch.*, 1908, 10, 283—299).—The electrochemical nature

of ferments is considered to be proved. Invertin and pepsin are adsorbed in all reactions by clay, and in none by kaolin; they therefore have the character of acids. In neutral and alkaline fluids, malt-diastase is not adsorbed by kaolin, but in acid fluids it is; it is therefore amphoteric, but with stronger acid than basic properties. Corresponding with this, it is completely adsorbed by clay when neutral or alkaline, and only incompletely when acid. Ptyalin and trypsin are also amphoteric, being adsorbed by both clay and kaolin under all conditions of reaction.

W. D. H.

The Identity of Pepsin and Rennin. OLOF HAMMARSTEN (*Zeitsch. physiol. Chem.*, 1908, 56, 18—80).—A long critical and experimental examination of the much-debated point as to whether or not pepsin and rennin are identical. The conclusion reached is that they are not, and the most striking proof of this is that solutions of each ferment were prepared from which the other was absent. If lead acetate or, better, magnesium carbonate is added to the mixture, both ferments are precipitated, but the precipitate of pepsin is more insoluble and the ferment is destroyed; extracts of the precipitate then contain practically only rennin. If, on the other hand, the original mixture is heated to a little over 40°, the rennin is destroyed rapidly, but the pepsin is destroyed less rapidly, and so can be obtained free from rennin.

W. D. H.

Systematic Investigation of Oxydases. OCTAVE DONY-HÉNault (*Bull. Acad. roy. Belg.*, 1908, 105—163. Compare Abstr., 1907, i, 1100).—The experimental methods used by Bertrand (Abstr., 1895, i, 385, 386; 1896, i, 534; ii, 61; 1897, i, 53; ii, 117, 338; 1898, i, 53; ii, 128; 1899, i, 313; 1904, i, 157) in his investigation of the ferment laccase of Japanese lac, and the conclusions this author draws from his results, are criticised, and evidence is brought forward in favour of the view that the oxidising action of laccase is really due, not to a specific enzyme, but to the presence of a manganous salt, the activity of which is stimulated by the action of hydroxyl ions.

When a solution containing a colloid and a manganous salt is precipitated by the addition of alcohol, the precipitate obtained contains some of all the constituents originally present in the solution, and this is the case even if the precipitation is repeated. Such precipitates exhibit feebly all the oxidising properties attributed to laccase and other oxidising ferments, and their activity can be greatly enhanced by the addition of minute traces of alkalis, so small as to be unrecognisable by the usual indicators. Bertrand's laccase is feebly alkaline, and always contains manganese, and its activity is practically paralysed in presence of acids. In view of these and other observations, it is contended that it is unnecessary to assume that Bertrand's laccase preparations, obtained by precipitating the latex of the lac tree by means of alcohol, contain any specific ferment, and that their oxidising action on quinol, pyrogallol, &c., is fully accounted for by the presence of an organic salt of manganese and the accidental presence of alkali. It is suggested, however, that these do not account for the oxidation of guaiacol by "laccase" and that some other

constituent, possibly an iron salt, intervenes in this instance. The results of a number of quantitative experiments on the oxidation of quinol by manganous salts, showing the influence of concentration, time, temperature, and other factors on this action, are tabulated in the original. It is also shown that animal charcoal rapidly oxidises quinol to benzoquinone in presence of air. It is also pointed out that too much stress is often laid on the mere inhibition of catalytic activity by the application of heat, as an indication of the presence of enzymes. For example, "laccase" becomes inactive at 100°, but there is good reason to believe that, in presence of colloids, organic manganous salts would decompose at this temperature and lose their oxidising activity. The oxidation of quinol to benzoquinone by salts of mercury, nickel, and other metals is possibly also due to their action in presence of alkalis or like impurities. T. A. H.

The Occurrence of Anticatalase in the Animal Organism. FR. BATTELLI and LINA STERN (*Biochem. Zeitsch.*, 1908, 10, 275—276). —Polemical against Vandervele and de Waele (this vol., i, 491). The present authors use the prefix anti- in the same sense as it is employed in the words antipepsin, antitrypsin, &c. W. D. H.

Rôle of the Reductase in Alcoholic Fermentation. WLADIMIR N. PALLADIN (*Bull. Acad. Sci. St. Petersburg*, 1908, [iv], 8, 667—672 *). —It is shown that both vegetable and animal reductase are directly concerned in alcoholic fermentation. The reduction of sodium selenite and of methylene-blue by zymin is retarded greatly by the addition of dextrose, and to a less extent by sucrose and galactose, but glycerol, lactose, and mannitol hasten the process of reduction.

An analogy is drawn between these processes and the selective assimilation by fungi of the more nutritive of two substances in a mixture, and also of *d*- rather than *l*-tartaric acid by certain bacteria. Z. K.

The Properties of Yeast Juice; the Zymase Formation in Yeast. EDWARD BUCHNER and FRITZ KLATTE (*Biochem. Zeitsch.*, 1908, 9, 415—435). —Fresh yeast juice has but small optical rotation, varying in Munich yeast between + 0.12° and - 0.28° and in Berlin yeast between + 1.68° and 2.48°. This activity appears to depend on the glycogen (of which $[\alpha]_D = +196$ —213°), for the rotation almost disappears on allowing the juice to ferment without addition of sugar. When sugar is added, the decrease in the dextrorotation does not correspond with its diminution as measured by collecting the carbon dioxide. In two cases, in spite of the disappearance of sugar, the rotation remained approximately constant. This phenomenon is possibly due to the concurrent formation of dextrorotatory polysaccharides. In the presence of disodium hydrogen phosphate, however, there was a decrease in the dextrorotation, which corresponded more nearly with the disappearance of the sugar.

Lange has shown that by keeping yeast for two hours in a solution

* and *Zeitsch. physiol. Chem.*, 1908, 56, 81-88.

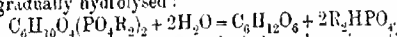
containing 0.1% asparagine and 4% potassium phosphate, with or without the addition of 10% sucrose, the fermentative power can be increased. Further experiments have shown that this treatment causes a regeneration of the zymase, and that the increased power is not due to the formation of fresh enzyme. The asparagite, furthermore, plays a very subordinate part, and the regeneration is due mainly to the presence of potassium dihydrogen phosphate; the corresponding dipotassium salt does not possess the like power.

S. B. S.

The Alcoholic Ferment of Yeast-Juice. III. The Function of the Phosphates in the Fermentation of Dextrose by Yeast-Juice. ARTHUR HARDEN and WILLIAM J. YOUNG (*Proc. Roy. Soc.*, 1908, 80, B, 299—311).—The addition of a phosphate to a fermenting mixture of dextrose and yeast-juice, not only produces a temporary acceleration in the rate of fermentation, but also an increased total fermentation. The last effect is due to the fact that the hexose phosphate formed during the period of temporary acceleration is continually hydrolysed by an enzyme with the production of free phosphate, which again enters into reaction and thus brings about fermentation. The reaction due to the phosphate can probably be represented as follows:

$$C_6H_{12}O_6 + 2R_2HPO_4 = 2CO_2 + 2C_6H_5O + C_6H_{10}O_4(PO_4R_2)_2 + 2H_2O$$

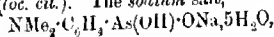
This reaction is only realised in the presence of ferment and co-ferment, phosphate alone being unable to bring about fermentation in presence of ferment and dextrose (*Abstr.*, 1907, i, 104). The hexose phosphate formed is gradually hydrolysed:



The conditions affecting this hydrolysis have been investigated; the rate at which it occurs, determines the rate of action when dextrose is fermented with yeast-juice. An optimum concentration of phosphate exists which produces a maximum initial rate of fermentation; an increase beyond this optimum diminishes the rate.

S. B. S.

***p*-Dimethylaminophenylarsonic Acid (Dimethylatoxyl).** AUGUST MICHAELIS (*Ber.*, 1908, 41, 1511—1516).—*p*-Dimethylaminophenylarsonic acid, previously prepared by the action of mercuric oxide and water on *p*-dimethylaminophenylarsenious oxide (*Abstr.*, 1902, i, 412), is now obtained by heating dimethylaniline with arsenic trichloride and treating the crude *p*-dimethylaminophenylarsenious oxide so formed with water, sodium hydroxide, and hydrogen peroxide, or by the action of methyl sulphate on aminophenylarsonic acid in sodium hydroxide solution. *p*-Dimethylaminophenylarsonic acid blackens when heated, and does not sublime as previously stated (*loc. cit.*). The sodium salt,



crystallises in leaflets.

(I. Y.)

An Isomeric Aminophenylarsonic Acid. ALFRED BERTHEIM (*Ber.*, 1908, 41, 1655—1657).—The nitrophenylarsonic acid described by Michaelis and Loesner (*Abstr.*, 1894, i, 187) may be reduced to the corresponding aminophenylarsonic acid, $NH_2 \cdot C_6H_4 \cdot AsO(OH)_2$, by

means of hydrogen sulphide (compare Michaelis, preceding abstract), provided that, after treating the solution of the nitro-compound in ammonium hydroxide with hydrogen sulphide, the product obtained on evaporating to dryness is extracted with hydrochloric acid, the extract rendered alkaline with sodium hydroxide, and then treated with a solution of copper sulphate. The reduction may also be performed with sodium amalgam. Whether this substance, which is isomeric with *p*-aminophenylarsonic acid (compare Ehrlich and Bertheim, Abstr., 1907, i, 812), is an ortho- or meta-compound has not been determined, although the latter is more probable. It crystallises in colourless prisms, m. p. 214°. It does not couple with diazobenzene or diazosulphanilic acid, but does so with *p*-nitrodiazobenzene, yielding a yellow dye, dissolving in alkalis with a red colour. It may itself be diazotised, and then forms *azo-dyes* with amines and phenols, which are soluble in sodium carbonate.

W. H. G.

Diazophenylarsonic Acid and its Products of Decomposition. ALFRED BERTHEIM (*Ber.*, 1908, 41, 1853—1857).—*p*-Diazophenylarsonic acid (Ehrlich and Bertheim, Abstr., 1907, i, 812) undergoes the usual diazo-decomposition. On boiling in acid solution, it yields *p*-hydroxyphenylarsonic acid, $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{AsO}(\text{OH})_2$, crystallising from dilute alcohol in white needles containing $2\frac{1}{2}\text{H}_2\text{O}$. *p*-Ethoxyphenylarsonic (phenetylarsonic acid) is obtained by diazotising the base, dissolved in absolute alcohol by means of hydrogen chloride, with ethyl nitrite. It has m. p. 185° (Michaelis, Abstr., 1902, i, 413, gives 209—210°). By acting on the diazo-compound with sodium hypophosphite, phenylarsonic acid is obtained, m. p. 158—162° (Michaelis gives 158°), and, by treating with copper powder, *p*-chlorophenylarsonic acid is formed, of which the barium salt was analysed. Treatment of the diazo-solution with cuprous cyanide, and hydrolysis of the resulting nitrile, furnishes *p*-carboxyphenylarsonic acid. Arsenious carboxyphenyl iodide has m. p. 172° (L. Coste, Abstr., 1881, 903, gives m. p. 153°).

J. C. C.

Preparation of Acyl Derivatives of *p*-Aminophenylarsonic Acid. [KURATORIUM DER GEORG UND FRANZISKA SPEYERSCHEN STUDIENSTIFTUNG] (D.R.-P. 191548).—Sodium *p*-aminophenylarsonate is readily acylated by the ordinary processes, and in this way the following derivatives have been obtained: *p*-formylaminophenylarsonic acid, slender needles, soluble in methyl alcohol or hot water, and *p*-acetylaminophenylarsonic acid, leaflets; the *phthalyl*-, *butyryl*-, *chloroacetyl*-, *benzoyl*-, and *malonyl*-*p*-aminophenylarsonic acids are similar compounds. The carbonyl derivative, $\text{CO}[\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{AsO}(\text{OH})_2]_2$, was also prepared.

G. T. M.

Some Homologues and Derivatives of Arsanilic Acid. I. LUDWIG BENDA and ROBERT KUHN (*Ber.*, 1908, 41, 1672—1678. Compare Ehrlich and Bertheim, Abstr., 1907, i, 812; O. and R. Adler, this vol., i, 492).—Homologues of aniline not substituted in the para-position readily condense with arsenic acid when heated at 170—200°, yielding substituted arsanilic acids; at the same time,

aromatic cacodylic acids of the type $\text{AsO}(\cdot\text{Ar}\cdot\text{NH}_2)_2\cdot\text{OH}$ are obtained as by-products. All the substituted arsanilic acids obtained give white silver salts. The amino-group may be acetylated and diazotised; the diazo-compounds couple with amines and phenols, yielding azo-dyes soluble in alkalis. The diazo-group is also readily replaceable by hydroxyl and halogens. The acetyl derivatives of the methyl homologues of arsanilic acid yield the corresponding carboxylic acids on oxidation.

6-Aminotolyl-3-arsonic acid, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{AsO}(\text{OH})_2$, obtained from arsenic acid and *o*-toluidine, crystallises in hexagonal prisms, m. p. 195° ; the acetate, $\text{C}_9\text{H}_{12}\text{O}_4\text{NAs}$, crystallises in brittle needles and prisms, decomposing at 306° .

5-Aminotolyl-2-arsonic acid, $\text{C}_7\text{H}_{10}\text{O}_3\text{NAs}$, from arsenic acid and *m*-toluidine, crystallises in long, rectangular prisms, m. p. 180° ; the acetate forms prismatic crystals, decomposing above 240° .

5-Amino-*p*-xylyl-2-arsonic acid, $\text{C}_8\text{H}_{10}\text{O}_3\text{NAs}$, from *p*-xylylene and arsenic acid, crystallises with $1\text{H}_2\text{O}$ in compact, hexagonal plates; the anhydrous substance has m. p. 215° ; the acetate, $\text{C}_{10}\text{H}_{14}\text{O}_4\text{NAs}$, forms compact, prismatic crystals, decomposing at 278° .

1-Naphthylamine-4-arsonic acid, $\text{NH}_2\cdot\text{C}_{10}\text{H}_7\cdot\text{AsO}(\text{OH})_2$, from arsenic acid and α -naphthylamine, forms small prisms, m. p. 173° .

3-Chloro-4-aminophenylarsonic acid, $\text{NH}_2\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{AsO}(\text{OH})_2$, from *o*-chloroaniline and arsenic acid, forms white crystals, m. p. 305° .

o-Cresol-5-arsonic acid, $\text{C}_6\text{H}_3\text{Me}(\text{OH})\cdot\text{AsO}(\text{OH})_2$, is prepared by diazotising 1-methyl-2:5-arsanilic acid and boiling the aqueous solution of the diazo-compound; it crystallises with $1\text{H}_2\text{O}$ in white prisms and needles, m. p. 180° ; the anhydrous substance has m. p. 222° .

W. H. G.

The Magnesium Derivatives of the Aromatic Chloro-compounds. A. HESSE (D.R.P. 189476).—In the Grignard reaction, chloro-derivatives behave quite differently from the bromo- and iodo-compounds, the latter readily react, giving rise both to alkyl and aryl magnesium halides, but aryl magnesium chlorides have not hitherto been produced by the ordinary methods. By the intervention of a more reactive alkyl halide, the reaction with magnesium may be started, and then this metal combines with the aromatic chloro-derivative.

Magnesium tolyl, benzyl or cymyl chloride can be produced by adding magnesium to an ethereal solution of ethyl bromide and, then introducing chlorotoluene, benzyl chloride, or chlorocymene, or, conversely, the magnesium alkyl halide (from methyl bromide, ethyl iodide, &c) may be added to an ethereal solution of the aromatic chloro-derivative in the presence of the requisite amount of magnesium.

G. T. M.

Organic Chemistry.

Estimation of Active Hydrogen in Organic Compounds. TH. ZEREWITINOFF (*Ber.*, 1908, 41, 2233—2243. Compare Abstr., 1907, ii, 509).—An extension of the method previously described to the determination of the number of replaceable hydrogen atoms in hydroxy-, thiol-, amino-, and imino-compounds. Frequently the results obtained are high, owing to the development of heat from the formation of the compound of pyridine and magnesium methiodide, and the further interaction of the pyridine and iodide with evolution of gas. The mixture is therefore cooled after the first evolution of gas has occurred. Care should also be taken that no barium oxide is introduced with the dry pyridine.

Ten hydroxy-compounds of the flavone type have been examined, and good results obtained even where the hydroxyl group is in the ortho-position; thus euxanthone is shown to contain two and haematoxylin five hydroxyl groups. The method also succeeds with mercaptans, such as the propyl, isobutyl, or phenyl derivatives, and with imido-compounds, such as succinimide, oxanilide, or phthalimide (compare Hibbert and Sudborough, *Trans.*, 1904, 85, 933). The acid amides, like acetamide, react in the cold with one mol. of magnesium methiodide, and on heating at 85° with another mol.; the error due to the action of the pyridine is estimated by carrying out a blank experiment. Aldehyde ammonia is shown in this way to have three active hydrogen atoms, two of which react in the cold. Carbamide and thiocarbamide have only three instead of four active hydrogen atoms, and phenylcarbamide, phenylthiocarbamide, and menthonesemicarbazone have two such hydrogen atoms; in all these cases the compound contains two amino- or one amino- and one imino-groups attached to the same carbon atom.

The reaction has been applied to tautomeric compounds, such as acetylacetone and ethyl acetoacetate, and at 100° these possess one active hydrogen atom; malonic acid contains three replaceable hydrogen atoms.

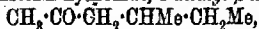
W. R.

Methylethylisobutylmethane [$\beta\beta$ -Dimethylhexane]. LATHAM CLARKE (*J. Amer. Chem. Soc.*, 1908, 30, 1144—1151).—In continuation of the work on the octanes (Abstr., 1907, i, 169), $\beta\beta$ -dimethylhexane has been synthesised by two different methods.

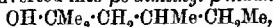
When methyl isobutyl ketone, prepared by the hydrolysis of ethyl isopropylacetoacetate, is treated with magnesium ethyl bromide, $\beta\beta$ -dimethyl- δ -hexanol, $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CMe}(\text{OH})\cdot\text{CH}_2\text{Me}$, b. p. 151°/768 mm., is produced. On converting this compound into the corresponding iodide and reducing the latter with zinc and hydrochloric acid, $\beta\beta$ -dimethylhexane, $\text{CH}_2\text{Me}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CHMe}_2$, b. p. 109°8—110°/762 mm., is obtained as an odourless, mobile liquid with D_4^{20} 0.7083, and n_D^{20} 1.3986.

When ethyl sec.-butylacetoacetate, b. p. 210—211°/762 mm., is

hydrolysed with potassium hydroxide, δ -methyl- β -hexanone,



b. p. $139^\circ/762$ mm., is produced, and on treatment with magnesium methyl iodide is converted into $\beta\delta$ -dimethyl- β -hexanol,

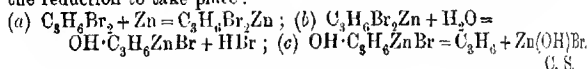


b. p. $150-150.5^\circ/766$ mm. If this carbinol is converted into the iodide and the latter reduced with zinc and hydrochloric acid, $\beta\delta$ -dimethylhexane is obtained, identical with the compound prepared by the first method.

β -CHloro- δ -methyl- $\Delta^{\alpha\beta}$ -amylene, $\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{CCl} \cdot \text{CH}_2$, b. p. $102.5-760$ mm., obtained by the action of phosphorus pentachloride on methyl isobutyl ketone, is a colourless, mobile liquid, and on oxidation with potassium permanganate yields isovaleric acid.

R. G.

Behaviour of Trimethylene Dibromide towards Zinc Dust and Acetic Acid. NICOLAI ZELINSKY and N. SCHLESINGER (*Ber.*, 1908, 41, 2429—2431).—After pointing out that no reaction occurs between glacial acetic acid and zinc dust, the authors state that carefully-dried trimethylene dibromide, glacial acetic acid, and zinc dust evolve with extreme slowness a gas which is found to be hydrogen, showing that a trace of water must still have been present. When 50% acetic acid is used, the gas which is evolved more rapidly, but still only slowly, proves to be cyclopropane, and not propane, which would be expected to be obtained. If the dibromide is gradually heated with glacial acetic acid, zinc dust, and concentrated hydrochloric or hydrobromic acid, the issuing gas consists of hydrogen free from hydrocarbon. As a result of these experiments, the authors consider that the first step in the reduction of trimethylene dibromide is the formation of a zinc additive compound, which is then decomposed by water; the latter must be present in not inconsiderable amount for the reduction to take place:



C. S.

Action of Metallic Oxides on Primary Alcohols. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1908, 146, 1376—1378).—The oxides examined fall into four classes: (1) those which undergo no reduction and which exert no appreciable effect on primary alcohols below 400° . This group includes titanium dioxide and the oxides of calcium, barium, strontium, magnesium, and silicon; (2) those rapidly reduced either to the metal or to a lower oxide; (3) oxides which are not reduced, but which decompose the alcohols catalytically, giving rise to hydrogen and an aldehyde, or to water and an ethylenic hydrocarbon, or to a mixture of aldehyde and hydrocarbon; (4) those oxides which are slowly reduced and at the same time exert a catalytic action.

W. O. W.

Action of Metallic Oxides on the Primary Alcohols (Case of the Reducible Oxides). PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1908, 147, 16—18).—As already stated (preceding abstract), primary alcohols are oxidised when passed over many

oxides heated below 400° . These oxides may be divided into four classes.

The simplest case is that in which the oxidation is limited to the formation of aldehyde and water, the oxide having no action on the aldehyde and the reduced oxide or metal having no catalytic power. The oxides of antimony and bismuth act in this way.

In the case of the more readily reducible oxides, the aldehyde formed is partly oxidised either to the corresponding acid or to carbon dioxide and water. Mercuric oxide is reduced by ethyl alcohol vapour at 150° , giving acetaldehyde and a large proportion of carbon dioxide, but not acetic acid. Manganese dioxide at 200° is reduced by ethyl alcohol to the sesquioxide, acetaldehyde being formed; at 250° , however, the sesquioxide formed is reduced, carbon dioxide and acetic acid being formed in addition to the aldehyde.

The third and largest class of oxides contains those of which the reduced metal or lower oxide has a catalytic action on the alcohol, the catalytic reaction being superposed on the initial oxidation. The oxides of nickel, cobalt, lead (PbO_2 , Pb_3O_4 , PbO), and copper (Cu_2O and CuO) at 350° belong to this class; the reduced metals have a dehydrogenating action on ethyl alcohol, giving acetaldehyde and hydrogen. In the case of nickel and lead oxides, but not with the copper oxides, acetic acid is produced. Manganese sesquioxide at 350° is slowly reduced by ethyl alcohol to the pale green manganous oxide, which decomposes ethyl alcohol into aldehyde and hydrogen. On the other hand, the yellow tungsten trioxide, WO_3 , at 350° is readily reduced by ethyl alcohol vapour, giving a blue intermediate oxide, which has a powerful dehydrating catalytic action, thus causing the formation of increasing amounts of ethylene besides the acetaldehyde, carbon dioxide, and acetic acid initially produced. Other oxides are reduced by alcohol vapour to lower non-reducible oxides, which are both dehydrating and dehydrogenating catalysts. Thus uranium trioxide, UO_3 , is reduced to UO_2 , and V_2O_5 to V_2O_3 , by alcohol vapour, giving aldehyde and carbon dioxide, whilst the reduced oxides act on further quantities of alcohol, giving aldehyde, hydrogen, ethylene, and water. In this class, the completion of the reduction is indicated by the disappearance of carbon dioxide in the gases produced.

The fourth class of oxides contains those which have themselves a catalytic action on alcohols. The latter is readily observed if the reduction is slow, but if this is rapid it is perceived only with difficulty. Thus ferric oxide, like alumina, is a dehydrating catalyst towards ethyl alcohol vapour, giving at 340° a mixture of ethylene and water, and being reduced to ferrous oxide and metallic iron. The latter, being a dehydrogenating catalyst, decomposes the alcohol into aldehyde and hydrogen. From this it follows that the proportion of ethylene gradually diminishes. Cadmium and stannous oxides, which are reduced very slowly by alcohol vapour at 340° , similarly act as dehydrogenating catalysts.

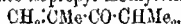
E. H.

Decomposition of Alcohols under the Catalytic Influence of Charcoal (Braise). GEORGES LEMOINE (*Compt. rend.*, 1908, 146, 1360—1366. Compare Senderens, *Abstr.*, 1907, ii, 218).—The author

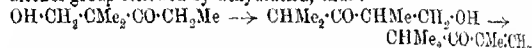
has examined the gaseous and liquid products formed when the state of vapour are passed over "quenched charcoal" (boulanger) heated to a temperature not exceeding 400° and usually below 385°. Methyl, ethyl, *n*-propyl, isopropyl, isobutyl, and amyl alcohol were treated in this way, and it was found in each case that the liquid product consisted of unaltered alcohol and substances having the reducing properties of aldehydes. Complete analyses of the gaseous products have been made, and it is found that hydrogen is always an important constituent of the mixture, except in the case of isopropyl alcohol, which becomes dehydrated with formation of trimethylene.

W. O. W.

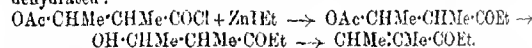
α -Dialkyl- β -keto-alcohols. Transformation by Dehydration. EDMOND E. BLAISE and I. HERMAN (*Compt. rend.*, 1908, 146, 1326—1328).—The transformation of ethyl hydroxypivalyl ketone, $\text{OH}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{COEt}$, into isopropyl methylvinyl ketone,



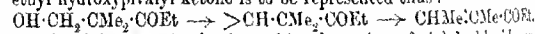
by the action of alkalis can be explained by a migration of the primary alcohol group followed by dehydration, thus:



or the dehydration may occur first and then a migration of the methyl group: $\text{OH}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{CO}\cdot\text{CH}_2\text{Me} \rightarrow >\text{CH}\cdot\text{CMe}_2\cdot\text{CO}\cdot\text{CH}_2\text{Me} \rightarrow \text{CH}_2\cdot\text{CMe}\cdot\text{CO}\cdot\text{CHMe}_2$. From the second hypothesis, it would be expected that the action of dehydrating agents would be similar to that of alkalis. When ethyl hydroxypivalyl ketone is treated with phosphoric oxide, however, the product is not isopropyl methylvinyl ketone, but another unsaturated ketone. The latter is identical with the ketone formed when β -acetoxy- α -methylbutyryl chloride is treated with ethyl zinc iodide and the product saponified and dehydrated:



It is therefore ethyl tiglyl ketone, $\text{CHMe}\cdot\text{CMe}\cdot\text{COEt}$, has b. p. 52°/15 mm., and gives a *p*-nitrophenylhydrazone, m. p. 134°, and a semicarbazone, m. p. 161—162°. Its formation by dehydration of ethyl hydroxypivalyl ketone is to be represented thus:



Ethyl tiglyl ketone is also formed by the action of tiglyl chloride on ethyl zinc iodide.

The conclusion is drawn that the action of alkalis on ethyl hydroxypivalyl ketone is represented by the first of the above schemes, the dehydration being preceded by the transposition. E. H.

Basic Properties of Oxygen. DOUGLAS MCINTOSH (*J. Amer. Chem. Soc.*, 1908, 30, 1097—1104).—Baeyer and Villiger (*Abstr.*, 1901, i, 658; 1902, i, 112, 355), in studying the basic properties of oxygen, have prepared a large number of compounds of organic substances with ferrocyanic acid. In order that the acid should be attached to the oxygen base in the simplest possible way, 4 mols. of the latter should unite with 1 mol. of the former, but in many of the

compounds described this ratio does not exist. For this reason, and also since water may have been present in the salts, an investigation has been made of the compounds of ferrocyanic acid with methyl and ethyl alcohols, acetone, and ether. A study of the vapour pressure of the products obtained by the absorption of ether and acetone by the acid has shown that they are not quadrivalent oxygen compounds, but solid solutions. With ethyl alcohol, a crystalline compound, m. p. -45° , containing 35.7% of the acid was obtained, and with methyl alcohol a compound, m. p. -33° , containing 37% of the acid. These compounds contain about 10 mols. of the alcohol to one of the acid, and are much more complex than those obtained by Baeyer and Villiger; their properties indicate that they are molecular compounds in which the alcohols are present as alcohol of crystallisation.

Acetic acid dissolves in liquid hydrogen bromide and hydrogen iodide with development of heat and formation of crystalline substances. The hydrogen bromide compound, m. p. 5° , contains 46–49% HBr. Tschitschibabin (Abstr., 1907, i, 276) has described a compound, $2C_2H_5O_2 \cdot HBr$, m. p. $7-8^{\circ}$. The hydrogen iodide compound, m. p. -50° , contains 59–70% HI.

Methyl ethyl ether unites with liquid hydrogen bromide and hydrogen iodide to form white, crystalline compounds, $MeEtO \cdot HBr$ and $MeEtO \cdot HI$, m. p. -30° and -22° . If these compounds have the constitution $\begin{matrix} Me \\ Et \end{matrix} > O < \begin{matrix} H \\ X \end{matrix}$, the oxygen atom is asymmetric. Attempts to separate them into optically active isomerides were not successful.

E. G.

Preparation of Methyl Sulphate. SOCIÉTÉ ANONYME DES PRODUITS CHIMIQUES DE FONTAINES IN LYON-MONPLAISIR (D.R.-P. 193830).—Methyl sulphate is conveniently prepared by adding chlorosulphonic acid (24 kilos.) to a mixture of 6.5 kilos. of methyl alcohol (90%) and 20 kilos. of carbon tetrachloride. After boiling off the diluent, the methyl sulphate is distilled under reduced pressure. A similar result is obtained on adding sulphur trioxide to the mixture of methyl alcohol and carbon tetrachloride.

G. T. M.

Reduction of Alkyl Nitrates to Nitrites in Alkaline Solution. AUGUST GUTMANN (Ber., 1908, 41, 2052–2056).—Nitrite and arsenate are formed when an alcoholic solution of amyl or ethyl nitrate is heated in a pressure flask at 100° with a solution of arsenious oxide in sodium hydroxide.

The author draws the conclusion that the presence of these products points to the intermediate formation of ethyl hydroperoxide: $NO_2 \cdot OEt + NaOH \rightarrow NO_2Na + EtO \cdot OH$ and $EtO \cdot OH + As(OH)_3 \rightarrow EtOH + AsO(OH)_2$.

Potassium cyanide and sulphide also reduce ethyl and amyl nitrates yielding potassium nitrite, potassium thiocyanate, and the alcohol. In this reaction, the author assumes the intermediate formation of ethyl hydroperosulphide: $NO_2 \cdot OEt + KSH \rightarrow KNO_2 + EtO \cdot SH$ and

$\text{EtO}\cdot\text{SH} + \text{KCN} \rightarrow \text{EtOH} + \text{KCNS}$. The sulphide solution used should be free from polysulphides and thiosulphate.

The reaction may be used in testing for alkyl nitrates in presence of the corresponding nitrites, as the latter do not give the yellow coloration and do not produce thiocyanates. J. J. S.

Character of the Compound formed by the Addition of Ammonia to Ethyl Phosphite-platochloride. CHARLES H. HERTY and R. O. E. DAVIS (*J. Amer. Chem. Soc.*, 1908, 30, 1084—1089).—Rosenheim and Levy (*Abstr.*, 1905, i, 183) have found that when dry ammonia is passed into a solution of triethyl phosphite-platochloride in benzene, the compound $\left[\text{Pt} \begin{smallmatrix} (\text{NH}_3)_2 \\ \text{P}(\text{OEt})_3 \end{smallmatrix} \right] \text{Cl}$ separates in white crystals, and that this salt is hydrolysed by water, forming an acid solution which exhibits abnormal molecular conductivity. The present authors, although following Rosenheim's method as closely as possible, have been unable to prepare this substance, but have obtained only the normal salt, $\left[\begin{smallmatrix} \text{Cl} \\ \text{Pt}(\text{NH}_3)_2 \\ \text{P}(\text{OEt})_3 \end{smallmatrix} \right] \text{Cl}$, which forms white crystals, and dissolves in water to give a neutral solution. Determinations of the molecular conductivity at 25° are recorded, and agree closely with the values obtained by Werner for all di-ionic complex ammonia compounds. E. G.

Molybdenum Compounds of Lecithin. RICHARD EHRENFELD (*Zeitsch. physiol. Chem.*, 1908, 56, 89—94).—Alcoholic lecithin solutions, when precipitated in the cold with an alcoholic nitric acid solution of ammonium molybdate, yield a substance, 10MoO_3 , 3 mols. of lecithin, when the lecithin is in excess, and 2MoO_3 , 1 mol. of lecithin, when the precipitant is in excess. A substance, $5[(\text{NH}_4)_6\text{Mo}_2\text{O}_{11}]$, 1 mol. of lecithin, is precipitated by an aqueous ammonium molybdate solution when there is a large excess of lecithin. G. B.

Preparation of Concentrated Formic Acid. CHEMISCHE FABRIK GRÜNAU, LANDSHOFF & MEYER (D.R.-P. 193509).—Although highly concentrated sulphuric or phosphoric acid acts destructively on formic acid, yet their acid salts decompose formates without exhibiting this action, and sodium hydrogen sulphate, when intimately mixed with dry sodium formate and heated in a retort, gives rise to 97—98% formic acid. G. T. M.

Hydrates of the Fatty Acids. D. E. TSAKALOTOS (*Compt. rend.*, 1908, 146, 1272—1274. Compare this vol., i, 498).—The constitution of the molecular combinations of acetic, propionic, and butyric acids with water is considered to be best represented by the formula $\text{R}\cdot\text{CO} \begin{smallmatrix} \text{H} \\ \text{O} \end{smallmatrix} \text{O} \begin{smallmatrix} \text{H} \\ \text{O} \end{smallmatrix}$.

The coefficients of viscosity of mixtures of formic acid with *m*-cresol are only slightly lower than the coefficients calculated from the rule of mixtures. Formic acid therefore shows less tendency than its homologues to form additive products with phenols. W. O. W.

Preparation of Phosphoric Esters from Phosphoric Oxide and the Diglycerides of Fatty Acids and their Bromo- and Iodo-derivatives. FERDINAND ULZER and J. BATIK (D.R.-P. 193189).—*Glyceryl distearophosphate*, $\text{PO}(\text{HO})_2 \cdot \text{O}-\text{C}_2\text{H}_5(\text{OCOC}_{17}\text{H}_{35})_2$, m. p. 58°, is obtained in almost quantitative yield by mixing together phosphoric oxide and melted distearin and slowly adding water. The corresponding oleyl derivative is oily. Glyceryl dibromodistearophosphate is a brown, viscid mass, having an acid number 109.3 and a saponification number 218.3. Other similar glycerides are referred to in the patent, all of which are obtained by the same general method of adding the requisite amount of water to an intimate mixture of phosphoric oxide and to the diglyceride of a fatty acid. G. T. M.

Catalytic Actions of Colloidal Metals of the Platinum Group. III. Reduction Catalysis with Colloidal Palladium and Platinum. CARL PAAL and JOSEF GERUM (*Ber.*, 1908, 41, 2273—2282. Compare *Abstr.*, 1905, ii, 397, 533; 1907, ii, 559; Willstätter, this vol., i, 383).—When the investigation was extended to unsaturated acids, it was found that the method applicable for the reduction of nitrobenzene did not lead to the conversion of sodium fumarate into succinate, but that when the salt and the hydrosol of palladium hydride are left together in a closed vessel filled with hydrogen, the gas is quickly absorbed.

In this way, fumaric, maleic, and cinnamic acids, as well as methyl cinnamate, have been reduced to the corresponding saturated acid and the rate of absorption measured. As a general rule, there is a little more hydrogen absorbed than that required by theory; this may be due to the metal, but in one case an aldehyde-like odour was observed, so that the reduction may proceed further than the acid. Palladium-black may be used, as also colloidal platinum, but the action is slower.

W. R.

Catalytic Actions of Colloidal Metals of the Platinum Group. IV. Reduction Catalysis with Colloidal Palladium. CARL PAAL and KARL ROTH (*Ber.*, 1908, 41, 2282—2291. Compare preceding abstract).—The reduction of oleic acid to stearic acid has been carried out at the ordinary temperature by Fokin (*Abstr.*, 1907, i, 819), and it may be accomplished by using sodium oleate and palladium hydrosol, the yield of pure stearic acid obtained being 60%. The method has been extended to the reduction of fats, the Hübl iodine value being used to determine percentage of unsaturated acids before and after. The fats used were castor oil, olive oil, and cod-liver oil. A quantitative yield of saturated fats was obtained from the castor oil in the form of a white, hard, crystalline mass, sintering at 77°, m. p. 81°. Although three times the quantity of hydrogen required was absorbed by the olive oil, the reduction was not quite complete (iodine value before, 81—82; after, 9); the tallow has m. p. 47°. Cod-liver oil was very nearly completely reduced; the product obtained was crystalline, m. p. 43—45°. The method therefore appears to be the only one yet discovered for reducing the unsaturated glycerides in a fat at the ordinary temperature.

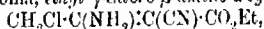
W. R.

Preparation of Glycollic Acid by the Electrolytic Reduction of Oxalic Acid. DEUTSCHE GOLD- UND SILBER-SCHNEIDANSTALT (D.R.P. 194038).—When oxalic acid is electrolysed in moderately concentrated sulphuric acid contained in an electrolytic cell fitted with a diaphragm and electrodes having a high supertension, a good yield of glycollic acid is produced. The following are details of this reduction. Cathode compartment, 700 parts of crystallised oxalic acid, 1100 parts of concentrated sulphuric acid, and 3300 parts of water; lead cathodes, current density 25 to 250 amperes per square metre; anode compartment, 30% sulphuric acid with an intermediate cell containing acid of the same strength. The temperature of the cathode solution was maintained above 25° throughout the electrolysis.

G. T. M.

Ethyl Chlorocycanoacetate and its Derivatives. ERICH BENARY (Ber., 1908, 41, 2399—2411).—Whilst chloroacetyl chloride reacts with ethyl sodiomalonate to form mainly ethyl tetrone-4-carboxylate (Abstr., 1907, i, 381), its behaviour with ethyl sodiocycanoacetate in dry ether leads smoothly to the formation of *ethyl γ-chloro-α-cycanoacetate*, $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$, m. p. 42—43°, which crystallises in colourless needles, has an acid reaction, develops a red coloration with ferric chloride, and is best purified by means of the green, crystalline copper salt, m. p. 171—172° (decomp.). The corresponding *methyl ester*, $\text{C}_6\text{H}_5\text{O}_2\text{NCl}$, m. p. 72—73°, forms a copper salt, which decomposes at 188—189°. Bromoacetyl bromide reacts with ethyl sodiocycanoacetate in a similar manner, yielding *ethyl γ-bromo-α-cycanoacetate*, $\text{C}_7\text{H}_5\text{O}_2\text{NBr}$, m. p. 59—61°, which has properties similar to those of the chlorinated compound; the copper salt has m. p. 163—164° (decomp.).

The dry silver salt of ethyl chlorocycanoacetate reacts with ethereal ethyl iodide to form *ethyl γ-chloro-α-cyano-β-ethoxycrotonate*, $\text{CH}_2\text{Cl}\cdot\text{C}(\text{OEt})\cdot\text{C}(\text{CN})\cdot\text{CO}_2\text{Et}$, m. p. 93—94°, which forms colourless needles, does not give a coloration with ferric chloride, and yields with alcoholic ammonia, *ethyl γ-chloro-β-amino-α-cyanocrotonate*,



m. p. 128—129°, in which the position of the amino-group is determined by the fact that the same compound is obtained by the action of ammonia on ethyl γ-chloro-α-cyano-β-methoxycrotonate.

Ethyl chlorocycanoacetate reacts with potassium cyanide in aqueous solution at 50—60° to form *ethyl α-dicyanoacetate*, $\text{CN}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$, m. p. 87—89°, in which the presence of the reactive methylene group enables the compound to condense with benzaldehyde and cinnamaldehyde, yielding the *benzylidene* and the *cinnamylidene* derivatives, the m. p. of which are 145—146° and 159—160° respectively; the latter is orange-coloured and the former yellow, having acid properties, and developing a blood-red coloration with ferric chloride.

The course of the reaction between ethyl chlorocycanoacetate and ammonia or organic bases in aqueous solution at the ordinary temperature depends on the base. Whilst with tertiary amines betaines are formed, and with ammonia, a pyrrolidone derivative,

secondary amines cause a simple replacement of the halogen, and primary amines, in addition, the formation of pyrrolidone derivatives; the production of the heterocyclic compound, however, does not occur in the case of primary aromatic amines. The addition of sodium hydroxide facilitates the preceding reactions. 4-Cyano-3:5-diketo-

pyrrolidine, $\text{NH} \begin{array}{c} \text{CH}_2 \cdot \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \quad \text{CH} \cdot \text{CN} \end{array}$, begins to decompose at 210° and melts

completely at $220-221^\circ$; the silver salt, $\text{C}_5\text{H}_3\text{O}_2\text{N}_2\text{Ag}$, crystallises in small needles. The compound is not attacked by boiling baryta, but is hydrolysed by boiling 30% potassium hydroxide, yielding the amide,

$\text{NH} \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{C} \cdot \text{CO} \cdot \text{NH}_2 \end{array}$, which decomposes at 215° . Ethyl α -cyano-

γ ethylaminoacetoacetate, $\text{NHEt} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}$, m. p. 225° , decomposition commencing at 215° , separates from hot water in long needles, reduces Fehling's solution, and forms a sodium salt and a hydrochloride, which decomposes at $173-174^\circ$. 4-Cyano-3:5-diketo- γ ethylpyrrolidine, obtained from the filtrate in the preceding preparation, darkens at 200° , and decomposes and melts completely at 228° ; the ammonium salt has m. p. $194-195^\circ$. Ethyl α -cyano- γ -anilinoacetoacetate, $\text{NHPh} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}$, decomposes at $212-213^\circ$; the hydrochloride has m. p. $182-183^\circ$ (decomp.). Ethyl α -cyano- γ -o-methoxyphenylaminoacetoacetate,

$\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}$, m. p. $207-208^\circ$, crystallises in white needles. Ethyl α -cyano- γ -piperidinoacetoacetate, $\text{C}_5\text{NH}_{10} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}$, decomposes at $215-216^\circ$, and forms a hydrochloride, m. p. $159-160^\circ$ (decomp.), a sodium salt, which darkens at 300° and has m. p. 310° (decomp.), and a copper salt, which decomposes at $226-227^\circ$. Ethyl α -cyano- γ -dimethylaminoacetoacetate, m. p. $208-209^\circ$ (decomp.), forms a hydrochloride, m. p. $143-144^\circ$, and a violet copper salt, which decomposes at $226-227^\circ$. The betaine of ethyl α -cyano- γ -trimethylaminoacetoacetate, $\text{NMe}_3 \begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{O} \end{array} \text{C} \cdot \text{C}(\text{CN}) \cdot \text{CO}_2\text{Et}$, m. p. $205-206^\circ$ (decomp.),

separates from hot water in hexagonal plates, and has a neutral reaction, bitter taste, and very feebly basic properties. The analogous pyridine derivative, $\text{C}_5\text{H}_5\text{N} \begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{O} \end{array} \text{C} \cdot \text{C}(\text{CN}) \cdot \text{CO}_2\text{Et}$, decomposes at $250-251^\circ$. All the preceding substances, obtained by the action of bases on ethyl chlorocyanoacetoacetate, reduce warm ammoniacal silver solutions and develop a red coloration with ferric chloride; the pyrrolidine derivatives are strongly acidic, whilst the others have a neutral reaction and very feeble acid properties.

Ethyl chlorocyanoacetoacetate and phenylhydrazine in aqueous solution yield Rupe's α -phenylhydrazino- β -acetylphenylhydrazine (Abstr., 1898, i, 572). C. S.

Potassium Ammonium Oxalate. PHILIPPE BARBIER (*Bull. Soc. chim.*, 1908, [iv], 3, 725-726).—Anhydrous potassium ammonium oxalate separates in colourless, slender needles when a concentrated solution of potassium oxalate is added to a saturated solution of

ammonium carbonate to which a small quantity of ammonia solution has been added. When potassium oxalate is replaced by sodium oxalate, no separation of the corresponding sodium ammonium oxalate occurs.

T. A. H.

Tautomerism of Succinyl Chloride. RICHARD MEYER and KARL MARK (*Ber.*, 1908, 41, 2459—2471. Compare Meyer and Jugilewitsch, *Abstr.*, 1897, i, 350).—From the investigation of Auger (*Abstr.*, 1888, 952), succinyl chloride is apparently a mixture of the symmetrical with the asymmetrical compound; nevertheless, on treating succinyl chloride with an alcohol, the same ester is obtained as by acting on silver succinate with the corresponding alkyl iodide. In no case was an isomeride isolated from the product formed from the succinyl chloride; this fact speaks for the tautomeric character of succinyl chloride (compare Emery, *Abstr.*, 1890, 236).

The following new esters of succinic and dibromosuccinic acid have been prepared:

Cetyl succinate, $C_2H_4(CO_2 \cdot C_{16}H_{33})_2$, crystallises in small, glistening leaflets, m. p. 58°. *p-Nitrobenzyl succinate*, $C_2H_4(CO_2 \cdot CH_2 \cdot C_6H_4 \cdot NO_2)_2$, crystallises in slender needles, m. p. 90°; the corresponding *o-nitrobenzyl* ester has m. p. 104—105°. *Cetyl dibromosuccinate*,

$C_2H_2Br_2(CO_2 \cdot C_{16}H_{33})_2$, has m. p. 36—37°. *Benzyl dibromosuccinate*, $C_2H_2Br_2(CO_2 \cdot CH_2Ph)_2$, forms short, stout crystals, m. p. 92—93°.

When succinyl chloride is heated with bromine at 140—150° in a flask fitted with a reflux condenser, the principal product formed is succinyl bromide; this reacts with benzene and aluminium chloride, yielding an *additive* product which is decomposed by water with the formation of dibromosuccinophenone (compare Paal and Schulze, *Abstr.*, 1902, i, 228).

The fraction, b. p. 115—127°, obtained during the fractionation of the impure succinyl bromide, prepared as just described, yields on treatment with benzene and aluminium chloride a mixture of dibromosuccinophenone and a *substance* crystallising in colourless leaflets, m. p. 97—100°.

Dibromosuccinophenone yields on treatment with phenylhydrazine a *substance* which probably has the formula $C_2H_2(CPh:N \cdot NPh)_2$; it softens at about 60°, and decomposes at 100°. Similarly, a *substance*, $C_2H_2(CPh:N \cdot NPh \cdot CH_2Ph)_2$, is obtained by acting on the ketone with *as*-phenylbenzylhydrazine; it crystallises in colourless needles, m. p. 109°.

W. H. G.

Ketens. X. Malonic Semichloride, Malonic Anhydride, and its Transformation into Keten. HERMANN STAUDINGER and E. ORT (*Ber.*, 1908, 41, 2208—2217. Compare this vol., i, 411).—In attempting to prepare malonyl chloride by acting on an ethereal solution of malonic acid with thionyl chloride, a product was obtained which proved to be malonic semichloride. It was thought possible that by acting on this compound with tertiary bases, the hitherto unknown unimolecular anhydride of malonic acid would be obtained.

Instead, however, *additive* products were formed of the type $C_3NH_5Cl \cdot CO \cdot CR_2 \cdot CO_2H \cdot NC_2H_5$. The product obtained from malonic semichloride decomposes when warmed, yielding a tarry substance; the products from the semichlorides of dimethyl- and diethylmalonic acid yield amorphous substances having the constitution

$$CR_2 \begin{array}{c} \diagup CO \cdot NC_2H_5 \\ \diagdown CO \cdot O \end{array}$$

When heated under reduced pressure, malonic semichloride yields acetyl chloride and carbon dioxide; the corresponding diethyl derivative yields α -ethylbutyryl chloride and carbon dioxide, whilst dimethylmalonic semichloride yields isobutyryl chloride, carbon dioxide, and dimethylmalonic anhydride. The latter compound was found to be identical with that described by Einhorn (this vol., i, 312) as a duodecimolecular anhydride of dimethylmalonic acid. It is insoluble in most solvents; in others it dissolves with decomposition, consequently the mol. wt. cannot be determined. The slight depression of the freezing point observed by Einhorn, which led to the belief in the existence of a duodecimolecular form, was undoubtedly due to the presence of impurity. The same also applies to diethylmalonic anhydride (Abstr., 1906, i, 398).

Both anhydrides, although undoubtedly highly polymerised, react as if unimolecular; thus, both compounds decompose when heated, yielding ketens: $CR_2(CO)_2O \rightarrow CO_2 + CR_2CO$.

Malonic semichloride, $COCl \cdot CH_2 \cdot CO_2H$, crystallises in small needles, m. p. about 65° (decomp.). It readily decomposes both at the ordinary temperature and when heated. *Dimethylmalonic semichloride*, $C_2H_5O_2Cl$, forms compact crystals, m. p. about 64 – 65° (decomp.), having a characteristic odour. The corresponding *diethyl* compound was obtained as an oil, which could not be solidified.

Dimethylmalonic anhydride (compare Einhorn, *loc. cit.*) is a slightly grey powder, which when rapidly heated decomposes at 170 – 175° . It decomposes when heated under a pressure of 12 mm. at 160 – 180° , yielding dimethylketen (compare Staudinger and Klever, Abstr., 1906, i, 234). The latter compound distills with slight decomposition at $34^\circ/750$ mm.; it has m. p. -97.5° , b. p. $48.5^\circ/12$ mm.

Diethylketen, CEt_2CO , prepared from diethylmalonic anhydride, is a liquid, b. p. 91 – $92^\circ/749$ mm., which solidifies to a yellow, crystalline mass at the temperature of liquid air. It is slightly more yellow than the dimethyl compound.

W. H. G.

Ferrous and Ferric Double Salts of Polybasic Acids. A. SCHOLZ (*Monatsk.*, 1908, 29, 439–450).—Whilst ferrous salts are usually green and ferric salts yellow, Eder and Valenta (Abstr., 1881, 713) found that oxalic acid forms a yellow potassium ferrous, but a green potassium ferric, salt. These results have now been confirmed, and double ferrous and ferric salts of malonic acid prepared and found also to have the usual colours reversed.

Potassium and ammonium ferrous malonates, $FeM'(C_3H_2O_4)_2 \cdot 2H_2O$ ($M' = K$ or NH_4), are prepared from ferrous iodide and potassium and ammonium malonates, and form yellow crystals which oxidise rapidly

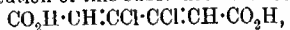
on exposure to air. A sodium ferrous malonate could not be prepared.

Potassium, sodium, and ammonium ferric malonates,

$\text{Fe}_2\text{M}'_6(\text{C}_3\text{H}_2\text{O}_4)_6 \cdot 4\text{H}_2\text{O}$ ($\text{M}' = \text{K}, \text{Na}, \text{or } \text{NH}_4$), are prepared from ferric hydroxide, malonic acid, and potassium, sodium, or ammonium malonate, and form emerald-green crystals which are readily soluble in water.

Attempts to prepare double salts of succinic, glutaric, and fumaric acids led to the formation of the known basic ferric salts; maleic acid yields a basic ferric salt, $\text{C}_4\text{H}_2\text{O}_4\text{Fe} \cdot \text{OH}$. G. Y.

Muconic Acid Derivatives. Constitution of Dichloromuconic Acid. DAN RADULESCU (*Chem. Zentr.*, 1908, i, 1832—1833; from *Bul. Soc. Stiinte Bucuresti*, 1907, 16, 191—206).—In view of the fact that when ethyl dichloromuconate is treated with sodium ethoxide a disodium compound is produced, and that Canizzaro's reaction yields diacetyl, the constitution of this substance must be



and the stability of the free acid, acid chloride, and amide points to

the configuration $\begin{array}{c} \text{Cl} \cdot \text{C} \text{---} \text{C} \cdot \text{Cl} \\ | \quad \quad | \\ \text{CO}_2\text{H} \cdot \text{C} \cdot \text{H} \quad \text{H} \cdot \text{C} \cdot \text{CO}_2\text{H} \end{array}$. Details are given for the

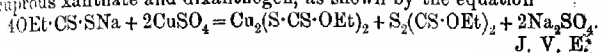
preparation of dichloromuconic acid chloride from a mixture of dry muconic acid and phosphorus pentachloride. It is a colourless, tasteless, and odourless substance, giving an *amide* which does not melt below 210° . An apparatus is described enabling the preparation and filtration of this ester to be performed in an atmosphere of an inert gas. J. V. E.

Preparation of Methylenecitric Acid. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 193767. Compare Abstr., 1904, i, 649).—The reactions formerly employed in preparing methylenecitric acid are more or less reversible, owing to the presence of water among the products. The condensation becomes complete when methylene derivatives, such as methylene sulphate, methyl methylenediacetate, or chloromethyl acetate, are employed which can condense without the elimination of water.

Anhydrous citric acid, when heated at $140\text{--}150^\circ$ with the calculated amount of methyl methylenediacetate and a few drops of concentrated sulphuric acid, yields pure methylenecitric acid, which is crystallised from boiling water. When methylene sulphate is employed, the condensation is effected in the presence of sodium acetate or glacial acetic acid. A good yield of methylenecitric acid is obtained when trioxymethylene condenses either with acetylcitric acid or with citric acid in the presence of acid chlorides or anhydrides. G. T. M.

Xanthic Acid. MANFRED RAGO (*Chem. Zeit.*, 1908, 32, 630—631, 654—656, 677—679).—In the reaction of a copper salt with an ethylxanthate, a brownish-black precipitate is obtained, the colour of which soon changes to yellow. It has frequently been suggested that cupric xanthate is first formed, which then is decomposed with

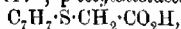
formation of the cuprous salt. The author has re-investigated this question, and comes to the following conclusions: (1) The yellow precipitate just referred to is cuprous xanthate. (2) Cupric xanthate is not formed in the reaction. The evanescent, brownish-black precipitate also formed initially consists mainly of cupric thiocarbonate. (3) This is due to the fact that in the preparation of the xanthate a certain proportion of thiocarbonate is also formed, owing to a reaction between alkali hydroxides and xanthates. (4) The author shows that the reaction between an alkali xanthate and a cupric salt yields cuprous xanthate and dioxanthogen, as shown by the equation



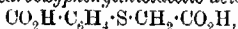
J. V. E.

Preparation of Dithioglycollic Acid and Arylthioglycollic Acids. KALLE & Co. (D.R.-P. 194039, 194040).—When aqueous solutions of sodium disulphide and sodium chloroacetate are mixed in the cold, there is little or no deposition of sulphur. The mixture becomes warm, and, after heating to boiling, the solution contains sodium dithioglycolate.

When thioglycollic acid is treated with a soluble diazo-salt, a diazo-derivative, $\text{R}\cdot\text{N}_2\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, of this acid is produced as an insoluble, crystalline precipitate, which, on heating, loses nitrogen and gives rise to an arylthioglycollic [arylthiolacetic] acid, $\text{R}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$. The following have been prepared: *phenylthiolacetic acid*, $\text{SPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, colourless needles, m. p. 117° ; *p-tolylthiolacetic acid*,



needles, m. p. 93° ; *o-carboxyphenylthiolacetic acid*,



obtained from diazotised anthranilic acid; *α -naphthylthiolacetic acid*, white needles.

G. T. M.

Preparation of Formaldehydesulphoxylate. BADISCHE ANILIN- & SODA FABRIK (D.R.-P. 194052).—Normal zinc sulphite, in aqueous solution, when treated successively with zinc dust and formaldehyde at 100° furnishes a sparingly soluble basic zinc formaldehydesulphoxylate, $\text{ZnSO}_3 + \text{Zn} + \text{CH}_2\text{O} + \text{H}_2\text{O} = \text{CH}_2\text{O}\cdot\text{ZnSO}_3 + \text{Zn}(\text{OH})_2$. Ammonium sulphite, when treated similarly, furnishes ammonium formaldehydesulphoxylate.

G. T. M.

Inversion of Sucrose by Invertase. C. S. HUDSON (*J. Amer. Chem. Soc.*, 1908, 30, 1160—1166).—O'Sullivan and Thompson (*Trans.*, 1899, 51, 834) have found that the inversion of sucrose by invertase is a unimolecular reaction, and have shown that the results of other observers who held the opposite view were vitiated by a systematic error in their polarimetric measurements. This error is due to the fact that the dextrose formed is initially in a birotatory state, and therefore the optical activity of a solution undergoing inversion does not indicate the amount of inversion which has taken place. If, however, alkali hydroxide is added to the solution and the optical activity is allowed to become constant, the true amount of inversion

which has taken place at the moment of adding the alkali is accurately indicated.

In the present paper, an account is given of a study of this question, and data are quoted which show that the inversion of sucrose by acids is a unimolecular reaction, even in its first stages, and that the polarimetric measurement of the inversion of sucrose by invertase involves a large source of error which can be obviated by adding alkali hydroxide to the solution before each reading. When this source of error is eliminated, as was done by O'Sullivan and Tempson, the inversion follows the unimolecular order.

E. C.

Formation of Molasses. SERGIUS SEBEDEFF (*Zeitsch. Ver. deut. Zuckerind.*, 1908, 599—621).—In order to trace the causes of molasses formation, the effect of some non-sugar constituents of molasses on the solubility of sucrose has been determined. Betaine has a slight salting-out effect at 30°, but at higher temperatures (50—70°) it increases the solubility of sucrose, and potassium glutamate (the other chief non-sugar constituent of molasses) increases the solubility of sucrose both at low and at higher temperatures.

G. B.

Action of Formaldehyde on Starch. ALBERT REICHARD (*Chem. Zentr.*, 1908, i, 1834—1835; from *Zeitsch. ges. Brauwesen*, 1908, 31, 161—163).—Solutions of formaldehyde lower the temperature at which starch gelatinises. In the same space of time, a 2% formaldehyde solution of starch was completely gelatinised at 59°, and a 37% solution at 49°. If left a sufficiently long time, gelatinisation is completed at the ordinary temperature.

J. V. E.

Gum of the Almond Tree. R. HUERRE (*J. Pharm. Chim.*, 1908, [vi], 27, 561—569).—This gum differs from that of the closely-related apricot and plum trees in containing a small proportion of matter soluble in water (10—20% instead of 80—90%). Nevertheless, there is a close chemical relationship, all three consisting largely of pentosans, yielding arabinose on hydrolysis. From the almond tree gum, galactose has now, in addition, been isolated.

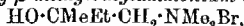
G. B.

Decomposition Curves of some Nitrocelluloses of American Manufacture. OSWIN W. WILCOX (*Zeitsch. angew. Chem.*, 1908, 21, 1407—1411).—During an investigation of the stability of ordinary collodion wool by Obermüller's method (*Abstr.*, 1905, ii, 391), the author has found that the amount of decomposition in a definite interval of time is greater when the gaseous decomposition products are left in contact with the sample during the preceding interval than when they are removed. From an examination of the curves, it appears that a given sample of nitrocellulose, when heated at 140°, has a characteristic decomposition pressure; as the heating is continued, a new component or phase is produced, which reinforces the previous one by its decomposition pressure; the pressure increase then remains more or less constant until a new phase is again produced, and so the process repeats itself.

P. H.

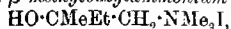
Preparation of the Alkyl Halides of Dialkylaminodimethylethylcarbinol and their Benzoyl Derivatives. J. D. RIEDEL (D.R.P. 195813).—The dialkylaminodimethylethylcarbinols and their benzoyl derivatives, when treated with alkyl halides, furnish quaternary salts which have valuable therapeutic properties.

Trimethyl-β-hydroxy-β-methylbutylammonium bromide,



colourless spicules, m. p. 163—169°, is produced by adding methyl bromide to dimethylaminodimethylethylcarbinol; its benzoyl derivative (stovaine methobromide) forms colourless needles.

Trimethyl-β-hydroxy-β-methylbutylammonium iodide,



colourless prisms, m. p. 123—125°, and its benzoyl derivative, needles, m. p. 169—170°. *Dimethylethyl-β-hydroxy-β-methylbutylammonium bromide*, $\text{HO} \cdot \text{CMeEt} \cdot \text{CH}_2 \cdot \text{NMe}_2 \text{EtBr}$, its benzoyl derivative, the corresponding quaternary ethiodide, and its benzoyl derivative, needles, m. p. 155—157°, are prepared similarly.

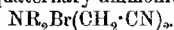
G. T. M.

Synthesis of Alanine and α-Aminobutyric Acid. NICOLAI D. ZELINSKY and GEORG STADNIKOFF (*Ber.*, 1908, 41, 2061—2063).—α-Aminopropionitrile hydrochloride is obtained in a 23%, together with alanine in a 40%, yield from acetaldehyde by the authors' method for the synthesis of aminonitriles. In the same manner, α-aminobutyronitrile hydrochloride is obtained in a 25%, together with α-aminobutyric acid in a 29.4%, yield from propaldehyde. In support of the authors' view of the mechanism of the reaction, experiments are quoted showing that α-aminophenylacetonitrile and α-amino-cyclohexylacetonitrile are formed from benzaldehyde and cyclohexanone respectively only in the presence of water.

G. Y.

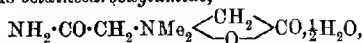
A New Synthesis of isoLeucine. WALTHER BRASCH and ERNST FRIEDMANN (*Beitr. chem. Physiol. Path.*, 1908, 11, 376—380).—sec-Butylmalonic acid, $\text{CHMeEt} \cdot \text{CH}(\text{CO}_2\text{H})_2$, yields on bromination the α-derivative, $\text{CHMeEt} \cdot \text{CBr}(\text{CO}_2\text{H})_2$, which, when heated, is converted into α-bromo-β-methylvaleric acid, $\text{CHMeEt} \cdot \text{CHBr} \cdot \text{CO}_2\text{H}$; this, when left in contact with concentrated ammonia solution, yields α-amino-β-methylvaleric acid, $\text{CHMeEt} \cdot \text{CH}(\text{NH}_2) \cdot \text{CO}_2\text{H}$, or isoleucine. S. B. S.

Betainecarboxylic Acids and Betainecarboxyamides. JULIUS VON BRAUN (*Ber.*, 1908, 41, 2123—2129).—Bromoacetonitrile unites with tertiary aminoacetonitriles which do not contain an aromatic group to form quaternary ammonium salts,

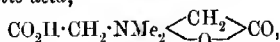


When these are shaken with silver hydroxide, not only is the bromine replaced by hydroxyl, but at least one of the cyanomethyl groups undergoes change, and on removing silver from the solution with hydrogen sulphide and evaporating, quantitative yields of betainecarboxyamides, $\text{NH}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{NR}_2 \cdot \text{CH}_2 \cdot \text{CO}$, are obtained. On hydrolysis, these are converted into the corresponding betainecarboxylic acids.

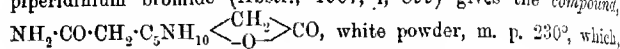
s-Di- ω -cyanotetramethylammonium bromide, $\text{NMe}_2\text{Br}(\text{CH}_2\text{CN})_2$, prepared from dimethylaminoacetonitrile and bromoacetonitrile in the cold, forms glistening crystals, m. p. 135° (decomp.), this with silver hydroxide yields *betainecarboxylamide*,



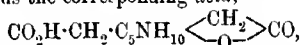
white powder, m. p. 122° , and this on hydrolysis with hydrochloric acid furnishes the *chloride*, $\text{NMe}_2\text{Cl}(\text{CH}_2\cdot\text{CO}_2\text{H})_2$, white, crystalline powder, m. p. 207° , which, on treatment with silver hydroxide, gives *betainecarboxylic acid*,



white, crystalline powder, m. p. 245° . Similarly, *biscyanomethylpiperidinium bromide* (Abstr., 1907, i, 899) gives the *compound*,

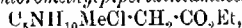


white powder, m. p. 230° , which, on hydrolysis, yields the corresponding *acid*,



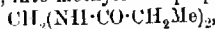
white powder, m. p. 249° ; the *chloride*, $\text{C}_9\text{H}_{18}\text{O}_4\text{NCl}\cdot 2\text{H}_2\text{O}$, crystallises in rosettes of needles, m. p. 137° (decomp.); the anhydrous salt has m. p. 200° ; the *bromide*, $\text{C}_9\text{H}_{18}\text{O}_4\text{NBr}\cdot 2\text{H}_2\text{O}$, crystallises in shining needles, m. p. $147\text{--}148^\circ$.

The compound $\text{C}_5\text{NH}_{10}\text{Me}\left\langle\begin{array}{c}\text{CH}_2 \\ \text{O}\end{array}\right\rangle\text{O}$ (Klages and Margolinsky, Abstr., 1904, i, 145) was prepared as follows: ethyl iodomethylpiperidiniumacetate (Wedekind and Oechslen, Abstr., 1902, i, 392) is converted into *ethyl chloromethylpiperidiniumacetate*,



m. p. 189° , which gives a *platinichloride*, small, yellowish-red crystals, m. p. 225° , and, on treatment with hydrochloric acid, furnishes the required compound. The *chloride*, $\text{C}_5\text{NH}_{10}\text{MeCl}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, has m. p. 213° (decomp.), and the *platinichloride* forms small, reddish-yellow crystals, m. p. 219° . J. C. C.

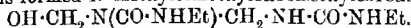
N-Methylol Compounds of Acid Amides. II. ALFRED EINHOEN [and, in part, RICHARD FEIBELMANN, MAX GÜTLER, ALEXANDER HAMBURGER, and EDUARD SPRÖNGERTS] (*Annalen*, 1908, 361, 113—165. Compare Abstr., 1906, i, 245).—The *N*-methylol compounds of propionamide, isobutyramide, and dipropylacetamide have been prepared in amplification of the earlier paper. *N*-Methylolpropionamide, $\text{CH}_3\text{Me}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{OH}$, is readily converted by alkalis at the ordinary temperature into *N*-methylolmethylenebispropionamide, $\text{OH}\cdot\text{CH}_2\cdot\text{N}(\text{CO}\cdot\text{CH}_2\text{Me})\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\text{Me}$, or, when heated gently with acids, into methylenebispropionamide,



whilst on oxidation with chromic acid and sulphuric acid, it yields formylpropionamide, $\text{CHO}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\text{Me}$. As with benzoylethylamide, attempts to prepare an *N*-methylol derivative of isovalerylethylamide have been unsuccessful. Urethane forms an *N*-methylol compound, $\text{OH}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}_2\text{Et}$, which behaves in the same manner as

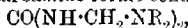
N-methylolpropionamide, being converted by alkalis into *N*-methylol-methylenebisurethane, $\text{OH}\cdot\text{CH}_2\cdot\text{N}(\text{CO}_2\text{Et})\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}_2\text{Et}$, and by acids into methylenebisurethane (Conrad and Hock, Abstr., 1903, i, 605).

Whilst carbamido forms mono- and di-methylol derivatives (this vol., i, 141), a methylol ethylcarbamide could not be obtained, but in its place is formed *N*-methylolmethylenebisethylcarbamide,



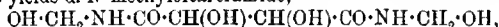
Both dimethylcarbamides, on the other hand, yield monomethylol compounds, $\text{NMe}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{OH}$ and $\text{NHMe}\cdot\text{CO}\cdot\text{NMe}\cdot\text{CH}_2\cdot\text{OH}$ respectively. This is remarkable, as monoalkylamides do not form methylol compounds. In acid solution, the dimethylcarbamides yield methylene derivatives, $\text{CH}_2(\text{NH}\cdot\text{CO}\cdot\text{NMe}_2)_2$ and $\text{CH}_2(\text{NMe}\cdot\text{CO}\cdot\text{NHMe})_2$.

Triethylcarbamido does not form a methylol derivative; this and the fact that *s*-dimethylcarbamido forms a mono-, but not a di-, methylol derivative may be looked upon as evidence in favour of the ψ constitution for carbamides, $\text{OH}\cdot\text{C}(\text{NEt})\cdot\text{NEt}_2$ and $\text{OH}\cdot\text{C}(\text{NMe})\cdot\text{NHMe}$. Like other acid amides, carbamide forms condensation products,

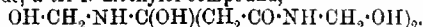


with formaldehyde and secondary bases.

Also the amides of hydroxy-carboxylic acids form *N*-methylol compounds; these contain one methylol for each amide group; lactic acid yields *N*-methylol-lactamide, $\text{OH}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{OH}$; tartramide yields di-*N*-methyloltartramide,



and citramide, a tri-*N*-methylol compound,



N-Methylol-lactamide and *N*-methylolmandelamide yield dibenzoyl derivatives in which the methylol hydroxyl, as well as that of the hydroxy-acid, is benzoylated. Methylol compounds of the amides of quinoline-6-carboxylic acid and camphocarboxylic acid are described.

N-Methylolpropionamide, $\text{C}_5\text{H}_9\text{O}_2\text{N}$, prepared in a 90% yield from propionamide and formaldehyde in presence of barium hydroxide, crystallises in colourless prisms, m. p. 64° , is hygroscopic, and when heated evolves formaldehyde. *N*-Methylolmethylenebispropionamide, $\text{C}_8\text{H}_{16}\text{O}_4\text{N}_2$, crystallises in rhomboids, m. p. $76-77^\circ$, does not evolve formaldehyde when boiled with water, and reduces Tollens's silver solution more slowly than the preceding substance. *Methylenebispropionamide*, $\text{C}_7\text{H}_{14}\text{O}_3\text{N}_2$, crystallises in needles, m. p. 201° , and remains unchanged when boiled with potassium chromate and sulphuric acid or when heated with bromine. *N*-Formylpropionamide, $\text{CH}_3\text{Me}\cdot\text{CO}\cdot\text{NH}\cdot\text{CHO}$, formed by oxidation of *N*-methylolpropionamide with chromic acid in sulphuric acid solution, crystallises in prismatic needles, m. p. 65° , decomposes when heated, and yields formylphenylhydrazide, m. p. 142° , when boiled with alcoholic phenylhydrazine.

N-Methylolisobutyramide, $\text{CHMe}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{OH}$, crystallises in needles, m. p. 77° .

α -Ethylbutyramide is best prepared by treating diethylmalonic acid with phosphorus trichloride, and the resulting ethylbutyryl chloride

with ammonia in ethereal solution. *Methylenebis- α -ethylbutyramide*, $\text{CH}_3(\text{NH}\cdot\text{CO}\cdot\text{CHEt}_2)_2$, prepared by the action of hydrochloric acid on equal amounts of α -ethylbutyramide and its *N*-methylol derivative (*loc. cit.*), forms needles, m. p. 235°. *α -Ethylbutyryldiethylglycylmethylenediamine*, $\text{CHEt}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{N}(\text{Et})_2$, formed by the action of *N*-methylol- α -ethylbutyramide on diethylglycylamide in concentrated sulphuric acid solution, crystallises in prismatic leaflets, m. p. 78—79°, and has very weak basic properties.

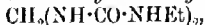
N-Methylol- α -propylvaleramide, $\text{CHPr}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{OH}$, formed from α -propylvaleramide and formaldehyde, crystallises in needles, m. p. 117°, evolves formaldehyde when heated, reduces Tollens's silver solution in a few minutes, and differs from the methylol derivatives of other amides of the fatty series by its insolubility in water.

isoValerylethylamide, $\text{CH}_2\text{Pr}\cdot\text{CO}\cdot\text{NHEt}$, prepared by the action of *iso*valeryl chloride on ethylamine and sodium hydroxide, has m. p. 20—30°, b. p. 121°/20 mm.

The action of formaldehyde and barium hydroxide on urethane leads to the formation of *N*-methylolurethane, $\text{C}_4\text{H}_9\text{O}_3\text{N}$, which is obtained in colourless prisms, m. p. 53°; it evolves formaldehyde when heated alone or in aqueous solution, and yields methylenebisurethane when treated with dilute hydrochloric acid. *N*-Methylolmethylenebisurethane, $\text{C}_8\text{H}_{16}\text{O}_5\text{N}_2$, crystallises from benzene in prisms, m. p. 68—69°, evolves formaldehyde when heated, and reduces silver solutions slowly.

Methylolcarbamide has m. p. 111° (116°: this vol., i, 142), and when treated with dilute hydrochloric acid forms di-*N*-methylolcarbamide or, on prolonged treatment, an amorphous substance, decomp. 260°. The action of concentrated hydrochloric acid on di-*N*-methylolcarbamide leads to the formation of a substance, $\text{C}_{12}\text{H}_{23}\text{O}_{12}\text{N}_3$, which crystallises in needles, not melted at 250°, and forms two hydrochlorides, crystallising from dilute hydrochloric acid in leaflets and from concentrated hydrochloric acid in strongly refracting, rhombic prisms respectively.

N-Methylolmethylenebisethylcarbamide, $\text{C}_8\text{H}_{18}\text{O}_5\text{N}_4$, prepared by gently heating ethylcarbamide with formaldehyde and barium hydroxide, crystallises in needles, m. p. 168—170° (decomp.), and evolves formaldehyde when heated. *Methylenebisethylcarbamide*,



formed by the action of concentrated hydrochloric acid on formaldehyde and ethylcarbamide, crystallises in small needles, m. p. 204°, and yields a *picrate*, crystallising in reddish-yellow needles, m. p. 115—116°.

N-Methylol-*as*-dimethylcarbamide, $\text{C}_4\text{H}_{10}\text{O}_2\text{N}_2$, prepared from *as*-dimethylcarbamide, crystallises in plates from alcohol or from ethyl acetate in needles, m. p. 110°, and evolves formaldehyde when heated. *Methylenebis-*as*-dimethylcarbamide*, $\text{C}_7\text{H}_{16}\text{O}_3\text{N}_4$, formed from *as*-dimethylcarbamide and formaldehyde in concentrated hydrochloric acid solution, crystallises in rhombic prisms, m. p. 183.5—184°.

N-Methylol-*s*-dimethylcarbamide crystallises in prisms, m. p. 99°, is hygroscopic, reduces silver solutions fairly rapidly, and evolves

formaldehyde when heated. *Methylenebis-s-dimethylcarbamide* crystallises from chloroform-ethyl acetate in prisms, m. p. 149—151°.

Condensation Products of Carbamide, Formaldehyde, and Secondary Bases.—*s-Tetraethyldiaminodimethylcarbamide*, $\text{CO}(\text{NH}\cdot\text{CH}_2\cdot\text{NEt}_2)_2$, prepared by heating carbamide with formaldehyde and diethylamine in aqueous solution, is obtained in a 35% yield as an oil, which decomposes on distillation in a vacuum. The *picrate*, $\text{C}_{23}\text{H}_{32}\text{O}_{15}\text{N}_{10}$, has m. p. 145—147°. *s-Dipiperidylldimethylcarbamide*,
 $\text{CO}(\text{NH}\cdot\text{CH}_2\cdot\text{C}_5\text{NH}_{10})_2$,

prepared from carbamide, piperidine, and formaldehyde in a 60% yield, crystallises from ethyl acetate in needles, m. p. 136°.

N-Methylol Compounds of Hydroxy-acid Amides.—*N-Methylol-lactamide*, $\text{C}_4\text{H}_9\text{O}_3\text{N}$, prepared by the action of formaldehyde and barium hydroxide on lactamide, crystallises from alcohol in colourless pyramids, m. p. 82—84°, and evolves formaldehyde when heated. The *dibenzoyl* derivative, $\text{OBz}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{OBz}$, formed by the action of benzoyl chloride on methylol-lactamide in pyridine solution, crystallises in needles, m. p. 124°. *Benzoyl-lactamide*,
 $\text{OBz}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NH}_2$,

formed from lactamide by Schotten-Baumann's method, crystallises in needles, m. p. 115°.

isoValerylactamide, $\text{C}_7\text{H}_{13}\text{O}_3\text{N}$, formed by the action of isovaleryl chloride on lactamide in pyridine solution, is obtained as a deliquescent mass or as a colourless oil, b. p. 157—158° in a vacuum.

Di-N-methyloltartramide, $\text{C}_6\text{H}_{12}\text{O}_6\text{N}_2$, from tartramide in a 70% yield, forms colourless crystals, m. p. 166°, and evolves formaldehyde when heated. When boiled with diethylamine in alcoholic solution, it forms *tetraethyldiaminodimethyltartramide*,
 $\text{C}_2\text{H}_2(\text{OH})_2(\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{NEt}_2)_2$,

which is obtained as an oil. The *dipicrate*, $\text{C}_{36}\text{H}_{36}\text{O}_{18}\text{N}_{10}$, forms yellow needles or leaflets, m. p. 155°. *Dibenzoyltartramide*,
 $\text{NH}_2\cdot\text{CO}\cdot\text{CH}(\text{OBz})\cdot\text{CH}(\text{OBz})\cdot\text{CO}\cdot\text{NH}_2$,

formed by the Schotten-Baumann method from tartramide, crystallises in needles, m. p. 240°.

Tri-N-methylolcitramide, $\text{C}_9\text{H}_{17}\text{O}_7\text{N}_3$, forms colourless prisms, m. p. 149—161° (decomp.), and evolves formaldehyde when heated.

N-Methylolmandelamide, $\text{OH}\cdot\text{CHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{OH}$, forms colourless crystals, m. p. 73—81° (decomp.), and evolves formaldehyde when heated. The *dibenzoyl* derivative, $\text{OBz}\cdot\text{CHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{OBz}$, formed from the methylol compound in pyridine solution, crystallises in slightly red needles, m. p. 110—115°. *Diethylaminomethylmandelamide*, $\text{OH}\cdot\text{CHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{NEt}_2$, prepared by boiling mandelamide, diethylamine, and formaldehyde in molecular proportions in alcoholic solution, is a basic oil; the *hydrochloride*, $\text{C}_{13}\text{H}_{20}\text{O}_2\text{N}_2\cdot\text{HCl}$, forms needles, m. p. 155°. *Piperidylmethylmandelamide*,
 $\text{OH}\cdot\text{CHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{C}_5\text{NH}_{10}$,

crystallises in colourless needles, m. p. 133—134°; the *hydrochloride*, $\text{C}_{14}\text{H}_{20}\text{O}_2\text{N}_2\cdot\text{HCl}$, forms needles, m. p. 188°.

Catecholdiacetamide (Carter and Lawrence, *Trans.*, 1900, 77, 1225)

was prepared by boiling catechol with chloroacetamide, sodium ethoxide, and sodium iodide in alcoholic solution; when treated with formaldehyde and potassium carbonate, it forms *di-N-methylol catecholdiacetamide*, $C_6H_4(O\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot OH)_2$, which separates in spherical crystals, m. p. 136—137°.

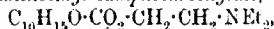
Resorcinoldiacetamide, prepared in the same manner as catecholdiacetamide, reacts with formaldehyde and potassium carbonate, forming *di-N-methylolresorcinoldiacetamide*, $C_{12}H_{16}O_6N_2$, which crystallises in microscopic needles, m. p. 192° (decomp.).

Additive Products of Halogenoacetamides and their Methylol Compounds with Hexamethylenetetramine.—The following additive compounds are described, $N_4(CH_2)_6\cdot R$.

R = Chloroacetamide: needles, m. p. 160° (decomp.); R = bromoacetamide: white needles, m. p. 170—171° (decomp.); R = iodoacetamide: leaflets, m. p. 166—167° (decomp.); R = methylolchloroacetamide: needles, m. p. 152° (decomp.); R = methylolbromoacetamide: needles, m. p. 155—158° (decomp.); R = methyloliodoacetamide: stellate needles, m. p. 150° (decomp.).

N-Methylol Compounds of Amides of Quinoline-6-carboxylic acid and Camphocarboxylic Acids.—*Quinoline-6-carboxylamide*, $C_{10}H_8ON_2$, prepared by the action of concentrated sulphuric acid on the corresponding nitrile, crystallises in yellow leaflets, m. p. 174°. The *ethiodide*, $C_{10}H_{12}ON_2I$, forms red or greenish-yellow crystals, m. p. 220° (partial decomp.). *Quinoline-6-carboxylmethylolamide*, $C_9H_8N\cdot CO\cdot NH\cdot CH_2\cdot OH$, prepared by the action of formaldehyde and potassium carbonate on the amide, forms colourless crystals, m. p. 179°, and evolves formaldehyde when heated. *Quinoline-6-carboxylpiperidylmethylamide*, formed from the amide, piperidine, and formaldehyde, crystallises in needles, m. p. 98°. The *hydrochloride*, $C_{10}H_{10}ON_2\cdot HCl$, forms colourless crystals, m. p. 192°, and is neutral in aqueous solution.

Camphocarboxylamide, $C_{10}H_{15}O\cdot CO\cdot NH_2$, prepared by the action of alcoholic ammonia on the ethyl ester at 140—150°, crystallises in colourless leaflets, m. p. 116—117°, and forms a *di-N-methylol* derivative, $C_{10}H_{15}O\cdot CO\cdot N(CH_2\cdot OH)_2$, which crystallises in colourless needles, m. p. 152—153°, and evolves formaldehyde when heated. It yields a *dibenzoyl* derivative, $C_{10}H_{15}O\cdot CO\cdot N(CH_2OBz)_2$, microscopic crystals, m. p. 95°. *Diethylaminoethyl camphocarboxylate*,



is formed by prolonged action of hydrogen chloride on diethylaminoethyl alcohol and camphocarboxylic acid in chloroform solution at the ordinary temperature; it crystallises from acetone in needles, m. p. 153° (decomp.). *Chloroethyl camphocarboxylate*, $C_{13}H_{19}O_3Cl$, formed in the same manner from the acid and chlorohydrin, is obtained as a colourless liquid, b. p. 190—191°/15 mm., having an odour of camphor. The *diethylamide*, $C_{10}H_{15}O\cdot CO\cdot NEt_2$, prepared by heating the ethyl ester with diethylamine at 110—120°, crystallises in colourless leaflets, m. p. 60—61°. The *piperidide*, $C_{10}H_{15}O\cdot CO\cdot C_5NH_{10}$, crystallises in colourless leaflets, m. p. 101°.

Action of Methylolchloroacetamide on β -Naphthol.—The action of methylolchloroacetamide on β -naphthol in alcoholic hydrogen chloride solution leads to the formation of 2-hydroxy-1-naphthylcarbonylchloro-

acetamide, $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$, which crystallises in colourless needles, m. p. 132° , and on hydrolysis with aqueous alcoholic hydrochloric acid yields 2-hydroxy-1-naphthabenzylamine (Betti, Abstr., 1906, i, 653). 2-Methoxy-1-naphthylcarbonylchloroacetamide, $\text{OMe}\cdot\text{C}_{10}\text{H}_6\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$,

formed from the hydroxy-compound by the action of methyl sulphate and potassium hydroxide, crystallises in needles, m. p. 170° , and on hydrolysis with boiling alcoholic hydrogen chloride yields 2-methoxy-1-naphthylcarbonylamine, $\text{OMe}\cdot\text{C}_{10}\text{H}_6\cdot\text{CH}_2\cdot\text{NH}_2$, crystallising in needles, m. p. about 100° ; the hydrochloride, m. p. 233° (decomp.); the hydrobromide, $\text{C}_{10}\text{H}_{13}\text{ON}\cdot\text{HBr}$, m. p. 242° (decomp.). The action of sodium nitrite on the hydrochloride leads to the formation of a nitroso-derivative of the corresponding alcohol, $\text{C}_{12}\text{H}_{11}\text{O}_3\text{N}$, which separates from alcohol in crystals, m. p. 112° . G. Y.

Carbethoxycarbimide. II. OTTO DIELS and ERNST JACOBY (*Ber.*, 1908, 41, 2393—2398. Compare Abstr., 1906, i, 237).—Attempts to prepare carbethoxycarbimido from potassium cyanate and ethyl chloro-carbonate led to the formation of only small amounts of the desired product, which is difficult to separate from the ethyl carbonate formed simultaneously (compare Wilm, Abstr., 1878, 851; Wurtz and Henninger, Abstr., 1885, 968). Carbethoxycarbimide is extremely stable at high temperatures, and could not be converted into Wurtz and Henninger's polymoride by heating. When treated with concentrated sulphuric acid, it is hydrolysed, yielding carbon dioxide and urethane, whereas with water, carbon dioxide and carbonyl-diurethane, $\text{CO}(\text{NH}\cdot\text{CO}_2\text{Et})_2$, are formed. Carbethoxycarbimide reacts energetically with amines, forming ethyl allophanates, $\text{NH}_2\text{R}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$, but with anthranilic acid, it yields carbon dioxide and the derivative, $\text{CO}_2\text{Et}\cdot\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$, which decomposes at 225° , and has acid properties, forming a crystalline potassium salt.

With alcohols, phenols, and oximes, carbethoxycarbimide reacts normally, forming iminodicarboxylic esters, $\text{CO}_2\text{R}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$, whilst with acetic anhydride, acetylurethane, $\text{NHAc}\cdot\text{CO}_2\text{Et}$, is formed, diacetylurethane, $\text{NAc}_2\cdot\text{CO}_2\text{Et}$, being probably the intermediate product. With phenol, carbethoxycarbimide forms a product, $\text{C}_{10}\text{H}_{11}\text{O}_4\text{N}$, which is obtained as a hygroscopic oil, b. p. $136\text{--}139^\circ$. *iso*-Nitrosomethyl propyl ketone and carbethoxycarbimide form a substance, $\text{C}_6\text{H}_{13}\text{O}_5\text{N}$, crystallising in small needles, m. p. $44\text{--}46^\circ$.

The action of hydrogen cyanide on carbethoxycarbimide leads to the formation of a product, $\text{CO}_2\text{Et}\cdot\text{NH}\cdot\text{CO}\cdot\text{N}(\text{CO}_2\text{Et})\cdot\text{CO}\cdot\text{CN}$ or

$\text{CO}_2\text{Et}\cdot\text{N} \begin{cases} \text{CO} \text{---} \text{N} \cdot \text{CO}_2\text{Et} \\ \text{C}(\text{NH}) \cdot \text{CO} \end{cases}$, which is obtained as a white, crystalline

powder, m. p. 125° (decomp.), has slight acid properties, and when dissolved in alkali and treated with carbon dioxide evolves hydrogen cyanide. G. Y.

Preparation of Soluble and Stable Additive Compounds of Thiocarbamide and Silver Salts. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 193661).—The double compounds of thio-

carbamide and silver salts hitherto known, which contain one atom of silver combined with one to three molecules of thiocarbamide, are sparingly soluble and readily decomposed. It has now been found that soluble and stable additive compounds may be produced by combining the components in the proportion of 1 atom of silver to 5 molecules of the base. The substance, $5\text{CH}_4\text{N}_2\text{S}\cdot\text{AgCl}$, is obtained by evaporating to dryness an aqueous solution of its components and crystallising the residue from alcohol. A similar product may be obtained from silver nitrate.

(I. T. M.)

Action of Iodine on Certain Thiocyanates. PAUL PFLEIFER and M. TILGNER (*Zeitsch. anorg. Chem.*, 1908, 58, 433—442).—The compound, $[\text{CoPy}_4(\text{SCN})_2]_2\text{I}_2$, prepared by boiling an alcoholic solution of tetrapyridinecobalt thiocyanate, $\text{CoPy}_4(\text{SCN})_2$, and iodine for one to two hours, separates from the solution on cooling in black, lustrous crystals, which lose about 2 mols. of pyridine and almost all the iodine on heating to 100° . The corresponding nickel compound, $[\text{NiPy}_4(\text{SCN})_2]_2\text{I}_2$, prepared by an analogous method, also occurs in lustrous, black crystals, which decompose slowly in the air, and behave like the cobalt compound when heated at 100° . Both compounds are additive products of iodine and the corresponding salts. An isomeric form of tetrapyridinecobalt thiocyanate, described by Sand (Abstr., 1903, i, 467) as being formed by the action of iodine on the ordinary form of the salt, does not appear to exist.

When triethylenediaminecobalt thiocyanate, $[\text{CoEn}_3](\text{SCN})_3$, is heated with iodine in alcoholic solution, the thiocyanate group is displaced by iodine, and from the solution the additive compound, $[\text{CoEn}_3]_3\text{I}_2$, separates in lustrous, deep black needles. The same compound is obtained by the action of iodine on triethylene diaminecobalt iodide, $[\text{CoEn}_3]\text{I}_3$; it is decomposed on boiling with dilute acids.

The compound, $[\text{Cr}(\text{NH}_3)_2(\text{SCN})_4]\text{NH}_4\text{I}$, first obtained by Nordenskiöld (Abstr., 1893, i, 290), has been prepared, and the above formula confirmed. As the halogens appear invariably to unite as molecules, it is probable that the compound in question has the doubled formula $\{[\text{Cr}(\text{NH}_3)_2(\text{SCN})_4]\text{NH}_4\}_2\text{I}_2$.

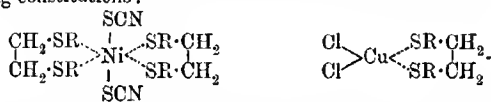
(G. S.)

Halogen Compounds of Molybdenum and Tungsten. IV. Thiocyanates of Tervalent Molybdenum. ARTHUR ROSENHEIM and ABRAHAM GARFUNKEL (*Ber.*, 1908, 41, 2386—2392. Compare Abstr., 1905, ii, 717; 1906, i, 603; 1907, i, 688).—A discussion of the constitution of the molybdenum salts described by Sand and his co-workers (Abstr., 1906, i, 487; this vol., i, 11, 397, 513). Maas and Sand's potassium salt, $[\text{Mo}(\text{SCN})_6(\text{OH}_2)]\text{K}_3\cdot 4\text{H}_2\text{O}$, is considered not to contain water or hydroxyl of constitution, and to be identical with Chilesotti's salt, $\text{K}_3\text{Mo}(\text{SCN})_6\cdot 4\text{H}_2\text{O}$ (Abstr., 1906, ii, 263, 365). When treated with thallium nitrate in aqueous solution, it forms an amorphous, light yellow precipitate, $\text{Tl}_2\text{Mo}(\text{SCN})_6$. It is found that the molybdenum of these salts can be oxidised by ammoniacal silver nitrate and the equivalent of the molybdenum calculated from the amount of silver liberated. The results obtained are sufficiently in agreement with those required by a trivalent molybdenum atom.

The metal-ammonium salts described by Sand and his co-workers must therefore be considered to be salts of the complex anion, $\text{Mo}(\text{SCN})_6^{4-}$. The zinc-ammonium salt on analysis gives figures agreeing with the formula $[\text{Zn}(\text{NH}_3)_4][\text{Mo}(\text{SCN})_6]_2$. Sand and Burger's pyridine salt, $6\text{C}_5\text{H}_5\text{N}, \text{H}_3\text{Mo}(\text{SCN})_6$ (Abstr., 1905, i, 923; 1906, i, 487), loses $3\text{C}_5\text{H}_5\text{N}$ over sulphuric acid in a vacuum, yielding a dark red salt, $3\text{C}_5\text{H}_5\text{N}, \text{H}_3\text{Mo}(\text{SON})_6$; 3 mols of pyridine must therefore be pyridine of crystallisation. Sand and Burger's tetra-pyridine salt is the dark red tripyridine salt crystallised with $3\text{H}_2\text{O}$.

G. Y.

Complex Compounds of Organic Disulphides. LEO A. TSCHUGAEFF (*Ber.*, 1908, 41, 2222—2226. Compare Abstr., 1906, i, 814, 984; 1907, i, 17, 392, 595, 830, 896; Werner, this vol., i, 440).—A survey of the previous work shows that the most stable complex metal compounds are those where penta-atomic rings are formed; the hexa-atomic rings are less stable, and there appears to be little or no tendency for other rings to be formed. Phillips (Abstr., 1901, i, 444) has shown that organic sulphides form double compounds with the salts of heavy metals, and the author has prepared and investigated the behaviour of disulphides of the general formula $\text{R}\cdot\text{S}\cdot[\text{CH}_2]_n\cdot\text{S}\cdot\text{R}$. The monosulphides do not give or give very unstable complexes with nickel or cupric salts; on the other hand, the disulphides, where $n=2$, give stable compounds with nickel thiocyanate and cupric chloride, where $\text{R}=\text{Me}$, Et , *isobutyl*, or *isoamyl*. In compounds where $n=0$, 1, 3, or 5, no such complexes are formed. The only exception so far found is $\text{Ph}\cdot\text{S}\cdot[\text{CH}_2]_2\cdot\text{S}\cdot\text{Ph}$, which does not give a complex compound with copper chloride or nickel thiocyanate. On the basis of Werner's co-ordination theory, these compounds are assigned the following constitutions:



The *ethyl* compound, $\text{Ni}(\text{SEt}\cdot[\text{CH}_2]_2\cdot\text{S}\cdot\text{Et})_2(\text{SCN})_2$, prepared by shaking the disulphide with an aqueous solution of the nickel salt for a few minutes, forms blue needles from 80—90% alcohol, and is quickly decomposed by water into its components. It loses half of its disulphide at 100° , and does not melt at 210° . The *methyl*,

$\text{Ni}(\text{SMe}\cdot[\text{CH}_2]_2\cdot\text{SMe})_2(\text{SCN})_2$, and *isoamyl*, $\text{Ni}(\text{SC}_5\text{H}_{11}\cdot[\text{CH}_2]_2\cdot\text{SC}_5\text{H}_{11})_2(\text{SCN})_2$, derivatives are similar.

The copper derivatives are prepared in a similar way in the presence of hydrochloric acid. The *ethyl* derivative,

$\text{Cu}(\text{SEt}\cdot[\text{CH}_2]_2\cdot\text{SEt})\text{Cl}_2$, forms dark green, almost black, prismatic needles, m. p. 113° ; the *isobutyl* compound is similar, m. p. 115° . They are more easily decomposed by water than the nickel compounds.

The diselenides appear to behave in a similar manner. W. R.

Cobalt Dioximines. III. New Complex Acid. LEO A. TSCHUGAEFF (*Ber.*, 1908, 41, 2226—2232).—One series of monobasic

salts has been described, which contain the cation $(\text{Co}2\text{aD}_2\text{H}_2)_2$ (Abstr., 1906, i, 814), and another series (Abstr., 1907, i, 904) of the general type $(\text{CoaXD}_2\text{H}_2)_2$, which are non-ionisable. [$\text{D} = \text{R} \cdot \text{C}(\text{NO} \cdot) \cdot \text{C}(\text{NO} \cdot) \cdot \text{R}$, $\text{a} = \text{ammonia or amine}$, $\text{X} = \text{an acidic radicle}$.] In accordance with the co-ordination theory, a third series should be capable of existence in which the cobalt group would be the anion, and this type has now been obtained.

Sodium cobaltidinitrodimethylglyoximate, $\text{Na}[\text{Co}(\text{NO}_2)_2\text{D}_2\text{H}_2]$, is obtained by digesting a 10% solution of sodium cobaltihexanitrite with excess of dimethylglyoxime until nitrous fumes cease to be evolved. After filtration, the salt crystallises out on evaporation:

$\text{Na}_2[\text{Co}(\text{NO}_2)_6] + 2\text{DH}_2 = \text{Na}[\text{Co}(\text{NO}_2)_2\text{D}_2\text{H}_2] + 2\text{NaNO}_2 + 2\text{HNO}_2$,
a reaction similar to the formation of the diamminochloride,
 $[\text{Co}2\text{NH}_3\text{D}_2\text{H}_2]\text{Cl}$,

from the luteo-salt, $[\text{Co}6\text{NH}_3\text{Cl}_6]$. The other salts described are obtained from this by double decomposition; the *ammonium* salt, $\text{NH}_4[\text{Co}(\text{NO}_2)_2\text{D}_2\text{H}_2] \cdot \text{H}_2\text{O}$, forms brownish-yellow needles; the *ethylammonium*, $\text{NH}_3\text{Et}[\text{Co}(\text{NO}_2)_2\text{D}_2\text{H}_2] \cdot \text{H}_2\text{O}$, *diisobutylammonium*, $\text{NH}_2(\text{C}_4\text{H}_9)_2[\text{Co}(\text{NO}_2)_2\text{D}_2\text{H}_2]$, *potassium*, *rubidium*, and *caesium* salts have been prepared. The *acid*, $\text{H}[\text{Co}(\text{NO}_2)_2\text{D}_2\text{H}_2] \cdot \text{H}_2\text{O}$, separates from a 5–10% solution of the sodium salt on the addition of hydrochloric acid as microscopic, hexagonal plates. It reddens litmus and decomposes carbonates, and from determinations of the molecular conductivity of the acid and its alkali salts, it is calculated that the mobility of the anion $[\text{Co}(\text{NO}_2)_2\text{D}_2\text{H}_2] = 18.0$ at 25° , and that the free acid is ionised to the extent of 88% at $\nu = 250$. The molecular conductivity of its aqueous solutions gradually decreases (thus $\nu = 250$, $\mu = 338.3$, after forty hours 320.0), due to the liberation of nitrous acid. It is fairly stable in the solid state in the air, but in a closed vessel it quickly decomposes, due perhaps to catalytic action of the nitrous acid. It rapidly loses water and nitrous acid at $100\text{--}110^\circ$. When an aqueous solution is gently warmed, a dark brown, crystalline precipitate of *cobaltinitroaquodimethylglyoximine*, $[\text{CoNO}_2\text{H}_2\text{O}\text{D}_2\text{H}_2]$, is produced. It is a non-electrolyte ($\mu = 3.0$, $\nu = 1000$), and the nitro group is firmly attached to the molecule.

Stable compounds containing the thiocyanate radicle instead of the nitro-group and less stable derivatives containing chlorine and iodine are under examination.
W. R.

Crystalline Compound of Magnesium Methiodide and Amyl Ether. TH. ZEREWITINOFF (*Lier.*, 1908, 41, 2244–2245).—The compounds of ether and magnesium alkyl iodides hitherto obtained are not crystallisable (Grignard, Abstr., 1901, i, 679; Blaise, 1901, i, 317; Baeyer and Villiger, 1902, i, 355; Tschelinzoff, 1906, i, 241), but when paraffin is added to the product obtained after interaction of 78–80 c.c. of amyl ether, 6 grams of magnesium, and 35.5 grams of methyl iodide, and the mixture left for some days, large, transparent crystals of the compound, $(\text{C}_5\text{H}_{11})_2\text{O} \cdot \text{MgMe}^{\text{I}}$, separate. They are unstable in the air.
W. R.

Synthesis of α -Hydroxymercuri-fatty Acids. I. Methyl Mercuridimalonate and its Product of Hydrolysis, Hydroxymercuriacetic Anhydride. WALTER SCHRAUTH and WALTER SCHORLLER (*Ber.*, 1908, 41, 2087—2094. Compare Fischer, this vol., i, 200).—The physiological importance of the α -amino-acids led to the idea of substituting different basic radicles for the amino-group and so forming other α -basic acids, which might be expected to have interesting physiological actions. The present paper is a study of the introduction of the hydroxymercuri-group, $\cdot\text{Hg}\cdot\text{OH}$, into the α -position in fatty acids.

Methyl mercuridimalonate, $\text{Hg}[\text{CH}(\text{CO}_2\text{Me})_2]_2$, is formed when methyl malonate suspended in water is gently heated and shaken with mercuric oxide; it crystallises from chloroform-ether in colourless plates, m. p. 127° (corr.), is readily soluble in organic solvents, is decomposed by halogens, forming the mercuric haloids, and yields mercuric sulphide when treated with ammonium sulphide. When shaken with *N*-sodium hydroxide, the mercuri-ester yields *hydroxymercuriacetic anhydride*,

$\text{Hg} \begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{O} \end{array} \text{CO}$, which is formed also by the action of mercuric oxide

on sodium malonate; it is obtained as a hard mass, which becomes brown at 200° , decomp. 250° (detonates). The *sodium* salt forms needles, is alkaline in aqueous solution, does not coagulate albumin, and does not yield mercury in contact with copper, but forms mercuric sulphide, as does also the anhydride, when treated with ammonium sulphide, and on electrolysis in alkaline solution deposits sodium amalgam at the cathode; this reaction is not reversible, as a mercury anode is not dissolved, and hence the mercury in sodium mercuriacetate is not ionised. The *copper* salt, $\text{Hg}_2\text{C}_4\text{H}_6\text{O}_8\text{Cu}$, was analysed; the *calcium*, *silver*, *lead*, and *mercuric* salts are white powders. The sodium and calcium salts act as antiseptics towards yeast; at the same time, the poisonous action of the mercury is much diminished. With hydrochloric acid, the anhydride forms mercuric chloride, but it is not attacked by cold dilute sulphuric acid, and when dissolved in nitric acid (D 1.2) and further diluted with water or alcohol, yields a white precipitate, which is probably the nitrate of mercuriacetic acid. Treatment of the anhydride with 10% ammonia leads to the formation of a yellowish-white, granular precipitate of varying and complicated composition.

When treated with anhydrous formic acid, the anhydride is converted into the *formate* of dihydroxymercuriacetylhydroxymercuriacetic acid, $\text{CHO}\cdot\text{O}\cdot\text{Hg}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{O}\cdot\text{Hg}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{O}\cdot\text{Hg}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, which is obtained as a colourless, crystalline substance, decomposing on exposure to light.

Attempts to isolate mercuridimalonic acid or mercuridiacetic acid as intermediate products in the hydrolysis of methyl mercuridimalonate were unsuccessful.

G. Y.

Ethylcyclobutane. NICOLAI ZELINSKY and J. GUTT (*Ber.*, 1908, 41, 2131—2434).—The scanty knowledge of cyclobutane hydrocarbons has induced the authors to commence an investigation of such compounds. The reaction between magnesium methyl iodide and

cyclobutanecarboxylamide leads to the formation of methyl cyclobutyl ketone, b. p. 136—136.5°/750 mm., n_D^{20} 1.4322, D_4^{20} 0.9112, D_4^{20} 0.9020 (compare Perkin, Trans., 1892, 61, 48), the semicarbazone of which has m. p. 148—149°. By reduction with sodium in moist ether at 0°, the ketone yields methylcyclobutylcarbinol, b. p. 144°/752 mm., n_D^{20} 1.14451, D_4^{20} 0.9075, of which the phenylurethane has m. p. 87.5—88°. When treated with hydriodic acid, D 1.96, the carbinol yielded an oily iodide which, without being isolated, was reduced by glacial acetic acid and zinc dust, forming a saturated hydrocarbon, C_6H_{12} , b. p. 72.2—72.5° (corr.), n_D^{20} 1.4080, D_4^{20} 0.7450; this is oxidised by nitric acid to succinic acid. The hydrocarbon is therefore ethylcyclobutane.

The authors are investigating methylcyclopentane, which closely resembles the preceding isomeric hydrocarbon, and is oxidised by nitric acid to succinic acid and not to glutaric acid, as would be expected.

C. S.

Occurrence of Nononaphthene in Coal Tar. FELIX B. AHRENS and LEO VON MOZDZĘNSKI (*Zeitsch. angew. Chem.*, 1908, 21, 1411—1414).—Xylene obtained from coal tar was found on nitration to yield an oil (b. p. 137—139°, D_4^{15} 0.7662) which had escaped nitration and proved on analysis to be nononaphthene, C_9H_{18} . Ten c.c. of this oil heated for eight hours at 125—130° with 50 c.c. of nitric acid, D 1.075, yielded on fractionation an oil, b. p. 125—135°/40 mm., which by means of alcoholic sodium hydroxide was shown to consist of a mixture of tertiary and secondary nitro-derivatives. The secondary nitro-derivative, $C_9H_{17}\cdot NO_2$, is a colourless oil which turns yellow; it has a characteristic pungent odour, and has b. p. 115—120°/15 mm., 220—224°/760 (decomp.), D_4^{20} 0.9778, and n_D^{20} 1.451; on treatment with bromine it yields an oil containing 31.74% of bromine. The tertiary nitro-derivative, $C_9H_{17}\cdot NO_2$, b. p. 102—105°/12 mm., 217—225°/760 (decomp.), D_4^{20} 0.9771, n_D^{20} 1.449, is a colourless oil which also turns yellow. The tertiary nitro-derivative when reduced by means of hydrochloric acid and tin foil yielded a mixture of amines which were separated by conversion into their picrates, one of which, A, was soluble in benzene, the other, B, being insoluble in benzene, but soluble in water. The picrate A crystallises in rhombic leaflets, m. p. 176—177°; when decomposed with potassium hydroxide and distilled with steam it yields an amine, $C_9H_{17}\cdot NH_2$, b. p. 175—176°/760 mm., D_4^{20} 0.8205, n_D^{20} 1.447; the hydrochloride, $C_9H_{17}\cdot NH_2\cdot HCl$, m. p. 155° (approx.); the oxalate, $C_{20}H_{40}O_4N_2$, white scales, darkens at 270° and decomposes without melting; the platinumchloride and aurichloride are oils which gradually solidify, but were not analysed. The picrate B, which separates from water in long crystals, m. p. 187—188°, yields an amine, $C_9H_{17}\cdot NH_2$, b. p. 172—173°/773 mm., D_4^{20} 0.8500, n_D^{20} 1.448, which yields a hydrochloride, glistening crystals from alcohol, m. p. 184—185°, an oxalate, $C_{20}H_{40}O_4N_2$, white, amorphous mass, which decomposes without melting at 265°, a platinumchloride, $(C_9H_{19}N)_2\cdot H_2PtCl_6$, orange-yellow, envelope-shaped crystals, decomp. 290°, and an aurichloride, which crystallises like the platinumchloride, m. p. 193—194° (decomp.).

The *secondary amino*, obtained by the reduction of the secondary nitro-derivative, has b. p. $175-177^{\circ}/748$ mm., D_4^{20} 0.8314, and n_D^{20} 1.446. Its *picrate* crystallises in four-sided plates, m. p. $173-174^{\circ}$; its *hydrochloride* is a liquid; its *platinichloride* forms glistening, yellow plates from water, decomp. 290° ; the *aurichloride* is an amorphous, sticky substance; the *oxalate* forms white, glistening scales, decomp. 265° .

On oxidation with nitric acid, D 1.075, nononaphthene is converted into succinic acid; oxidation with nitric acid, D 1.5, converts it into butyric acid.

When treated with moist chlorine at 30° in diffused daylight, nononaphthene yields a monochloro-derivative, which is a colourless liquid with a pungent odour, b. p. $103-104^{\circ}/40$ mm., D_4^{20} 0.9229.

Bromine in the presence of aluminium bromide or finely-divided iron converts nononaphthene into tribromo-*ψ*-cumene, m. p. 234° . P. H.

Isomeric Dihydrobenzenes and Optically Active Dihydro-toluene. NICOLAI D. ZELINSKY and A. GORSKY (*Ber.*, 1908, 41, 2479-2487).—An investigation on $\Delta^{1:2}$ - and $\Delta^{1:4}$ -cyclohexadienes and on 1-methyl- $\Delta^{2:4}$ -cyclohexadiene, carried out chiefly with the object of ascertaining the effect of ethylene linkings on the optical properties of compounds.

The conclusions of Markownikoff (*Abstr.*, 1899, i, 22) and Harries and Antoni (*Abstr.*, 1903, i, 613) are shown to be incorrect. The tetrabromide, m. p. 188° , is derived from $\Delta^{1:4}$ -cyclohexadiene, whilst the tetrabromide obtained from $\Delta^{1:2}$ -cyclohexadiene has m. p. $140-141^{\circ}$ (compare Crossley, *Trans.*, 1903, 83, 505).

Although $\Delta^{1:2}$ -cyclohexadiene and 1-methyl- $\Delta^{2:4}$ -cyclohexadiene contain contiguous double linkings, they do not follow Brühl's rule (*Trans.*, 1907, 91, 115). It is, however, not impossible that these compounds may have a dicyclic structure, since they do not readily form tetrabromo-derivatives, and are not readily oxidised.

$\Delta^{1:4}$ -cycloHexadiene has b. p. 85.5° (corr.), D_4^{20} 0.8471, D_4^{25} 0.8519, n_D^{20} 1.4729, mol. ref. 26.50 (compare von Baeyer, *Abstr.*, 1892, 1074; Brühl, *Abstr.*, 1894, i, 366). It readily forms a tetrabromide, m. p. 188° (corr.); the *dibromide*, $C_6H_8Br_2$, has m. p. 95° , b. p. about $105^{\circ}/15$ mm.

$\Delta^{1:2}$ -cycloHexadiene has b. p. 80.5° (corr.), D_4^{15} 0.8423, D_4^{20} 0.8376, n_D^{20} 1.4700, mol. ref. 26.66. It only combines readily with 1 mol. of bromine, forming a dibromide, m. p. $102-104$, b. p. about $105^{\circ}/14$ mm. (compare Crossley, *loc. cit.*). A small quantity of the *tetrabromide*, $C_6H_8Br_4$, is obtained by acting on the hydrocarbon with bromine in light petroleum; it crystallises in prisms, m. p. $140-141^{\circ}$ (corr.). The tetrabromide is not formed by acting on a solution of the dibromide with bromine in chloroform. $\Delta^{1:2}$ -cycloHexadiene when shaken with nitric acid (1.4) becomes violet, whilst $\Delta^{1:4}$ -cyclohexadiene when similarly treated undergoes violent oxidation.

1-Methyl- $\Delta^{2:4}$ -cyclohexadiene, C_7H_{10} , is obtained by the action of quinaldine on the dibromide of 1-methyl- Δ^3 -cyclohexene; it is a colourless liquid, b. p. $105.5-106^{\circ}$ (corr.), D_4^{15} 0.8324, D_4^{20} 0.8274, n_D^{20} 1.4680, $[\alpha]_D 36.42$. It is also obtained in small quantities by the action of

an alcoholic solution of potassium hydroxide on the dibromide, when it has n_D^{20} 57.48° (100 mm. tube). The principal product is, however, *ethoxymethylcyclohexene*, $C_8H_{16}O$; it is a colourless liquid, b. p. 169°/750 mm., D_4^{20} 0.8762, D_4^{25} 0.8746, n_D^{25} 1.4480, mol. ref. 42.72, n_D 18.56° (100 mm. tube).

1-Methyl- $\Delta^{2,4}$ -cyclohexadiene becomes violet-blue when shaken with nitric acid (1.4); it combines with 1 mol. of bromine, yielding a *dibromide*, $C_7H_{13}Br_2$, b. p. 107—108°/15 mm., n_D 33.2° (100 mm. tube); a tetrabromide could not be obtained.

W. H. G.

Lecture Experiments on the Preparation of Hydrocarbons. JAMES F. SPENCER (*Ber.*, 1908, 41, 2302—2303).—The author gives instructions for the preparation of benzene and naphthalene by the action of magnesium on the corresponding halogen derivative as already described (Spencer and Stokes, *Trans.*, 1908, 93, 68). Pentane or *isopentane* is prepared by heating amyl or *isomyl* iodide respectively with magnesium and adding water to the product.

J. C. C.

Derivatives of 2-Iodo-4-nitrotoluene with Polyvalent Iodine. CONRAD WILLGERODT and B. R. KOK (*Ber.*, 1908, 41, 2077—2083).—4-Nitro-*o*-toluidine hydrochloride, $C_7H_5O_2N_2 \cdot HCl$, forms white needles, blackens at 200°, m. p. 230° (decomp.).

2-Iodo-4-nitrotoluene crystallises in rhombic plates, m. p. 58° (51°; Reverdin, *Abstr.*, 1898, i, 180), and when treated with chlorine in chloroform solution is converted into the *iodochloride*, $NO_2 \cdot C_6H_4Me \cdot ICl_2$, which crystallises in sulphur-yellow prisms, decomp. 83°. The action of sodium carbonate and sodium hydroxide on this leads to the formation of 2-*iodoso*-4-nitrotoluene, $NO_2 \cdot C_6H_4Me \cdot IO$, which is obtained as an insoluble, yellowish-white powder, and explodes at 180—181°, having first changed into a mixture of the iodoxy- and iodo-compounds. 2-Iodoxy-4-nitrotoluene, $NO_2 \cdot C_6H_4Me \cdot IO_2$, formed by the action of hypochlorous acid on the iodoso-compound, is obtained as a white, flocculent precipitate, which explodes at 201°.

The following iodonium salts, $R = (NO_2 \cdot C_6H_4Me)_2I$, were prepared from a mixture of the iodoso- and iodoxy-compounds.

RCl : white needles, m. p. about 140°; RBr : decomp. 145°; RI : yellow needles, decomp. 113°; RNO_3 : white needles, m. p. 147°; $RHSO_4$: white needles, m. p. 165°; $R_2Cr_2O_7$: orange-yellow, amorphous precipitate, explodes 128°; R_2PtCl_6 : yellow leaflets, decomp. 180°.

*Phenyl-4-nitro-2-tolyl*iodonium hydroxide, $NO_2 \cdot C_6H_4Me \cdot IPh \cdot OH$, prepared by the action of silver oxide and water on a mixture of 2-iodoxy-4-nitrotoluene and iodosobenzene, is a strongly alkaline base. The following salts, $R' = NO_2 \cdot C_6H_4Me \cdot IPh$, are described.

$R'Cl$: white needles, m. p. 183°; $R'Br$: yellow, flocculent precipitate, m. p. 165°; $R'I$: yellow needles, decomp. 131°; $R'I_3$: dark brown prisms, m. p. 50°; $R'NO_3$: white prisms, m. p. 167° (decomp.); $R'H_2SO_4$: white prisms, m. p. 142°; $R'_2Cr_2O_7$: yellow powder, m. p. 137—138° (explodes); $(R'Cl)_2HgCl_2$: white needles, m. p. 157° (decomp.); R'_2PtCl_6 : yellowish-red prisms, m. p. 175° (decomp.).

4-Nitro-2-tolyl-*o*-tolylidonium hydroxide is prepared in the usual

manner from a mixture of 2-iodoxy-4-nitrotoluene and 2-iodosotoluene. The following salts, $R = NO_2 \cdot C_6H_4Me \cdot I(C_7H_7)$, are described.

RCl : white needles, m. p. 170° ; RBr : needles, m. p. 151° ; RI : decomp. 116° ; $R_2Cr_2O_7$: explodes 136° ; R_2PtCl_6 : golden leaflets, m. p. 158° ; $(RCl)_2HgCl_2$: needles, m. p. 168° . G. Y.

New Catalytic Effect of Aluminium Chloride. EYVIND BERTKER (*Bull. Soc. chim.*, 1908, [iv], 3, 726—729).—It is shown that when nitro-compounds are employed in the Friedel-Crafts reaction, the nitro-group is eliminated and that through its agency the condensation product formed is in part oxidised. In certain cases it is possible to nitrate compounds by using nitrates in the Friedel-Crafts reaction.

Trichloronitromethane reacts with benzene in presence of aluminium chloride to form triphenylmethane and some triphenylcarbinol, the latter being formed by oxidation of the hydrocarbon by the eliminated NO_2 group.

Ethyl nitrate reacts with benzene in presence of aluminium chloride to form nitrobenzene, the other possible products of the reaction, namely, ethyl chloride, ethylbenzene and nitroethylbenzene, being formed, if at all, only in minute quantity. With toluene the principal product is the *o*-nitro-compound, with small quantities of the para-isomeride. With benzaldehyde a vigorous reaction, apparently involving the $-CHO$ group, ensues, and *o*-nitrobenzaldehyde is not obtained. In these nitration reactions the hydrocarbon should be used in excess, and as water is always formed, considerable quantities of aluminium chloride are required. With benzene and amyl nitrite under similar conditions, some nitrosobenzene is formed, but the quantity is too small to be isolated. T. A. H.

Naphthalenesulphonates of Cerium. HUGO ERDMANN and THEODOR NIESZYTKA (*Annalen*, 1908, 361, 166—189. Compare Abstr., 1893, i, 651).—The cerium salts described were prepared by the action of the naphthalenesulphonic acids on cerium carbonate in aqueous solution and evaporation to crystallisation. The solubilities of the salts in water and methyl and ethyl alcohol are tabulated; the solubility increases with the number of sulphonic groups, but is small if a β -substituting group is present. The solubilities of cerium hydrogen naphthalene- β -sulphonate and the basic 1:5-disulphonate could not be determined, as the salts are unstable. The small solubility of cerium anthraquinonesulphonate is remarkable; the complete insolubility of cerium 8-hydroxynaphthalene-1-sulphonate and its characteristic colour allow of its utilisation in analysis.

Cerium naphthalene- α -sulphonate, $(C_{10}H_7O_3S)_3Ce$, crystallises in nacreous leaflets, has an acid reaction, and forms precipitates with ammonia, potassium hydroxide, potassium hydroxide and hydrogen peroxide, ammonium oxalate, and barium hydroxide or chloride in aqueous solution, or with benzidine in acetic acid solution, and a bluish-red precipitate with ammonium 1:8-hydroxynaphthalenesulphonate; these precipitations in aqueous solution are retarded by the presence of hydroxy-acids of the fatty series.

Cerium naphthalene-β-sulphonate, $(C_{10}H_7O_2S)_3Ce \cdot H_2O$, forms large, white leaflets, and gives similar precipitates to those of the α-salt.

Cerium naphthalene-1:5-disulphonate, $[C_{10}H_6(SO_3)_2]_2Ce \cdot \frac{1}{2}H_2O$, loses $\frac{1}{2}H_2O$ at 180° , and can be recrystallised without decomposing.

Cerium naphthalene-2:7-disulphonate, $[C_{10}H_6(SO_3)_2]_3Ce \cdot 3H_2O$, loses $3H_2O$ on prolonged exposure to air, more quickly in a desiccator, has a strong acid reaction, and with benzidine in hot acetic acid solution forms the benzidine salt.

Cerium naphthalene-2:6-disulphonate, $[C_{10}H_6(SO_3)_2]_2Ce \cdot H_2O$, loses $\frac{1}{2}H_2O$ at 135° , but H_2O at the ordinary temperature.

Cerium naphthalene-1:6-disulphonate, $[C_{10}H_6(SO_3)_2]_2Ce \cdot 4H_2O$, loses $4H_2O$ in a desiccator.

Cerium naphthalene-1:3:5-trisulphonate, $C_{10}H_3(SO_3)_3Ce \cdot \frac{1}{2}H_2O$, crystallises in white scales, loses its water of crystallisation in a desiccator, has an acid reaction, is decomposed slowly by hydrogen peroxide, and forms a precipitate with benzidine in aqueous hydrochloric acid solution.

Cerium naphthalene-1:3:6-trisulphonate ($\frac{3}{2}H_2O$) forms yellow scales and loses water slowly in a desiccator.

Cerium naphthalene-1:3:7-trisulphonate ($1\frac{1}{4}H_2O$) loses its water of crystallisation slowly on exposure to air.

Cerium 1-naphthol-8-sulphonate, $(C_{10}H_7SO_3)_3Ce \cdot 3H_2O$, formed from the ammonium sulphonate, forms a bluish-brown, amorphous precipitate, loses $3H_2O$ at 110° , has an acid reaction, is unstable, and dissolves in acids, forming bluish-red solutions. The action of the free naphtholsulphonic acid on cerium carbonate leads to the formation of a blue basic salt, $(C_{10}H_6SO_3)_3Ce_2$, which also dissolves in acids, forming bluish-red solutions.

Cerium chromotropate, $[C_{10}H_4(OH)_2(SO_3)_2]_2Ce \cdot 4H_2O$, formed from 1:8-dihydroxynaphthalene-3:6-disulphonic acid, is salted out of its solution; it forms a greyish-brown, microcrystalline mass, loses $4H_2O$ at 195° , has an acid reaction, and in concentrated solution commences only after some weeks to change into a basic salt, the edges of the solution becoming blue.

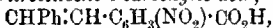
Cerium anthraquinonesulphonate, $(C_{14}H_9O_2SO_3)_3Ce \cdot 3H_2O$, forms green leaflets, loses $3H_2O$ at $187-195^\circ$, is very stable, has a strong acid reaction, and gives insoluble precipitates with benzidine, aniline, and toluidine. G. Y.

[Naphthalenesulphonates and Malonates of the] Rare Earths. HUGO ERDMANN and FRITZ WIRTH (*Annalen*, 1908, 361, 190—217).—See this vol., ii, 694.

The Stilbene Series. FRITZ ULLMANN and MEINRAD GOSCHWID (*Ber.*, 1908, 41, 2291—2297).—It is well known that a halogen atom in the benzene nucleus can readily be replaced by other substituents provided it is accompanied by a nitro-group in the ortho- or para-position; moreover, when the number of nitro-groups in the molecule is increased, the reactivity increases, and this is not diminished when, in the dinitro-derivatives, one nitro-group is replaced by a sulphonic, carboxylic, or aldehydic group. The authors have accordingly examined

the behaviour of negatively-substituted toluene derivatives and find that, when one of the nitro-groups in 2:4-dinitrotoluene is replaced by a carboxylic, sulphonic, or cyanogen group, the resulting compound condenses with benzaldehyde in presence of piperidine with the production of the corresponding stilbene derivatives just as 2:4-dinitrotoluene itself, under similar conditions, yields dinitrostilbene (Thiele and Escales, Abstr., 1901, i, 689). Further, 2:4:6-trinitrotoluene condenses with benzaldehyde more readily and at a lower temperature than do the disubstituted derivatives.

2-Nitrostilbene-4-sulphonamide, $\text{CHPh}\cdot\text{CH}\cdot\text{C}_6\text{H}_4(\text{NO}_2)\cdot\text{SO}_2\cdot\text{NH}_2$, prepared by condensing *o*-nitrotoluene-*p*-sulphonamide (Reverdin and Crépieux, Abstr., 1901, i, 685), forms yellow needles, m. p. 184°. It is readily reduced by stannous chloride and hydrochloric acid to **2-amino-stilbene-4-sulphonamide**, which crystallises from alcohol in colourless leaflets, m. p. 206—207°. Its solutions in glacial acetic acid or alcohol exhibit a blue fluorescence. The *acetyl* derivative forms stellate aggregates of white needles, m. p. 205°. **4-Nitrotoluene-2-sulphonamide** does not condense well with benzaldehyde, but **4-nitrotoluene-2-sulphonanilide**, m. p. 148°, prepared by condensing 4-nitrotoluene-2-sulphonyl chloride with aniline, readily condenses, forming **4-nitrostilbene-2-sulphonanilide**, which crystallises from glacial acetic acid in yellow needles, m. p. 206°. Similarly, *o*-nitro-*p*-toluonitrile furnishes **2-nitro-4-cyanostilbene**, $\text{CHPh}\cdot\text{CH}\cdot\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{CN}$, yellow needles, m. p. 170°, the *dibromo*-derivative, $\text{C}_{15}\text{H}_{10}\text{O}_2\text{N}_2\text{Br}_2$, of which forms colourless needles, m. p. 155—160° (decomp.). **2-Amino-4-cyanostilbene** forms pale yellow crystals, m. p. 123°; its solutions in benzene, acetic acid, and ether show a blue fluorescence, whilst that in alcohol is bluish-green. The *acetyl* derivative, colourless needles, has m. p. 220°. **2-Nitrostilbene-4-carboxylic acid**,



prepared by hydrolysis of the nitrile, crystallises from glacial acetic acid in small, yellow needles, m. p. 236°. It is also formed when ethyl 2-nitrotoluene-4-carboxylate is condensed with benzaldehyde, the ester being hydrolysed in the reaction.

2-Aminostilbene-4-carboxylic acid, prepared by reducing the nitro-compound, is a pale yellow, crystalline powder, m. p. 197—198°. Its solutions show a bluish-green fluorescence.

4-Nitro-2-cyanostilbene, prepared from *p*-nitro-*o*-toluonitrile, separates from glacial acetic acid in small, yellow needles, m. p. 142°. **2:4:6-Trinitrostilbene**, obtained from 2:4:6-trinitrotoluene, crystallises from glacial acetic acid in yellow, glistening needles, m. p. 156°. **2:4:6:4'-Tetranitrostilbene**, prepared by condensing 2:4:6-trinitrotoluene and *p*-nitrobenzaldehyde, forms yellow, glistening needles, m. p. 196°.

J. C. C.

Colourless and Coloured Triphenylmethyl. JULIUS SCHMIDLIN (*Ber.*, 1908, 41, 2471—2479. Compare this vol., i, 150; Gomberg, Abstr., 1907, i, 504; Tschitschibabin, Abstr., 1907, i, 1022).—A freshly-prepared solution of pure triphenylmethyl in benzene remains colourless for a few seconds and then gradually becomes orange-yellow. The colour of the solution disappears, however, when the latter is

shaken with air, reappearing again after a time, and again disappearing when agitated with air, until finally the solution remains permanently colourless. The conclusion is therefore drawn that the yellow solutions of triphenylmethyl contain both a coloured and a colourless form of triphenylmethyl. The two forms are convertible one into the other, and are present in solutions and in the solid substance in a definite state of equilibrium, which depends both on the nature of the solvent and on the temperature.

The disappearance and reappearance of the colour of solutions of triphenylmethyl is due to the fact that the coloured variety oxidises far more rapidly than the colourless form. On shaking an ethereal solution of triphenylmethyl with air, the yellow form is oxidised, yielding the peroxide, which being insoluble in ether may be filtered off; the colourless filtrate quickly becomes yellow, and on shaking yields a further quantity of peroxide. It is found from the amount of peroxide formed that an ethereal solution of triphenylmethyl contains roughly ten times as much of the colourless form as of the coloured form. The latter substance must consequently have an exceedingly intense colour.

The yellow form also absorbs iodine far more rapidly than the colourless form. When a quantity of iodine, slightly more than sufficient to combine with the triphenylmethyl present in the yellow form, is added to a solution of triphenylmethyl in chloroform, a reddish-brown solution is obtained. The colour of the solution slowly changes, and when a sufficient quantity of the yellow variety has been formed, the solution has the pure yellow colour of triphenylmethyl iodide.

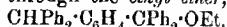
The state of equilibrium, triphenylmethyl (colourless) \rightleftharpoons triphenylmethyl (coloured), is displaced towards the left by lowering the temperature. A solution of triphenylmethyl in chloroform, which is orange-yellow at 15°, becomes quite colourless at -63°; the change in the colour intensity of a solution of triphenylmethyl iodide when similarly treated is barely perceptible.

W. H. G.

p-Benzhydryltetraphenylmethane. ALEXEI E. TSCHITSCHBAREK (*Ber.*, 1908, 41, 2421-2428).—In connexion with the constitution of triphenylmethyl, hexaphenylethane, $\text{CPh}_2\cdot\text{CPh}_2$, is a substance of great importance. Both Ullmann and Borsum (*Abstr.*, 1902, i, 755) and Gomberg (*Abstr.*, 1903, i, 214) thought they had obtained this hydrocarbon, the former by the action of zinc on triphenylchloromethane, and the latter by the polymerisation of triphenylmethyl. The behaviour of the hydrocarbon with bromine led the author to the view that it was *p*-benzhydryltetraphenylmethane, $\text{CPh}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHPh}_2$, (*Abstr.*, 1905, i, 125). He has now succeeded in definitely establishing this constitution. The stages of the proof are the following: Benzoyl chloride and triphenylmethane in the presence of aluminium chloride yield the well-known *p*-benzoyltriphenylmethane, the reaction of which with magnesium phenyl bromide leads to the formation of *p*-benzhydryltriphenylcarbinol, $\text{CHPh}_2\cdot\text{C}_6\text{H}_4\cdot\text{CPh}_2\cdot\text{OH}$; the condensation of the carbinol or its chloride and aniline hydrochloride in boiling glacial acetic acid results in the production of amino-*p*-benzhydryltetra-

phenylmethane hydrochloride, $\text{CHPh}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CPh}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2 \cdot \text{HCl}$, and from the sulphate by the replacement of the amino-group by hydrogen by the diazo-reaction, Ullmann and Borsum's "hexaphenylethane" is obtained, $\text{CHPh}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CPh}_2$.

A second modification of *p*-benzoyltriphenylmethane, m. p. 150° , is obtained by crystallisation from glacial acetic acid. *p*-Benzhydryl-triphenylcarbinol separates from alcohol in colourless crystals, m. p. 135 – 137° , but the crystals from other solvents obstinately retain benzene of crystallisation. The purification of the crude carbinol is therefore best effected through the ethyl ether,



m. p. 186° , which is obtained in nearly theoretical yield by adding a drop of acetyl chloride to the alcoholic solution of the carbinol. The chloride has m. p. 142° , becoming orange-coloured; the bromide melts at 140° to an orange liquid. Amino-*p*-benzhydryltetraphenylmethane, m. p. 195 – 198° (decomp.), is best purified through the hydrogen sulphate, m. p. 194 – 196° (decomp.). The diazo-sulphate, obtained by means of amyl nitrite in glacial acetic acid, decomposes at 120° , and by treatment with boiling alcohol yields *p*-benzhydryltetraphenylmethane and the ethyl ether of the phenol derived from the diazo-salt, m. p. 184° . C. S.

Preparation of Ethyl Phenylglycinate. GEORGES IMBERT UND CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE (D.R.P. 194884).—Ethyl phenylglycinate, $\text{NIPh} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, may be readily prepared by heating to boiling a mixture of ethyl chloroacetate, aniline, water, and calcium carbonate; carbon dioxide is evolved, and the fused product is separated from the calcium chloride solution. G. T. M.

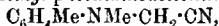
Action of Cyanogen Bromide and of Bromine on Aromatic Derivatives of Aminoacetonitrile. JULIUS VON BRAUN (*Ber.*, 1908, 41, 2100–2113).—In order to ascertain if the action of cyanogen bromide on arylaminoacetonitriles is similar to that observed in the case of the alkylamino-derivatives (*Abstr.*, 1907, i, 899), the author has selected the cases of methyl- and ethyl-anilinoacetonitrile, and finds that the interaction is quite different, the chief product in each case being the corresponding *p*-bromophenyl derivative. As by-products were obtained compounds of the formulae $\text{C}_{13}\text{H}_{13}\text{N}_4$ and $\text{C}_{20}\text{H}_{22}\text{N}_4$ respectively, the constitution of which has not yet been elucidated.

p-Bromophenylmethylaminoacetonitrile, $\text{C}_6\text{H}_4\text{Br} \cdot \text{NMe} \cdot \text{CH}_2 \cdot \text{CN}$, prepared by heating methylanilinoacetonitrile and cyanogen bromide in a closed vessel for five hours on the water-bath, has b. p. 205 – $206^\circ/22$ mm., m. p. 49° . On warming with 25% sulphuric acid, *p*-bromodimethylaniline is formed. The compound, $\text{C}_{13}\text{H}_{13}\text{N}_4$, crystallises from alcohol in colourless, glistening leaflets, m. p. 103° . It is hydrolysed by hydrochloric or sulphuric acid (25–38%) to an amino-acid, obtained as a dark viscous oil, and, on one occasion only, a substance was isolated which was probably trimethyldiaminodiphenylmethane.

s-ω-Dicyanotetramethylbenzidine, $\text{C}_{12}\text{H}_8(\text{NMe} \cdot \text{CH}_2 \cdot \text{CN})_2$, prepared from *s*-dimethylbenzidine and iodoacetonitrile, forms glistening,

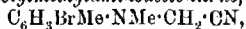
brown leaflets, m. p. 203° . *o*-Dicyanodiphenyldimethylethylene-diamine, $C_6H_4(NPh \cdot CH_2 \cdot CN)_2$, obtained from diphenylethylene-diamine and bromo- or iodo-acetonitrile, crystallises from alcohol in white leaflets, m. p. 131° . Neither this nor the foregoing substance is identical with the compound, m. p. 103° .

p-Bromophenylethylaminoacetonitrile, $C_6H_4Br \cdot NEt \cdot CH_2 \cdot CN$, prepared from ethylanilinoacetonitrile and cyanogen bromide, has b. p. $195^{\circ}/8$ mm. and m. p. 56° . On hydrolysis it yields *p*-bromomethyl-ethylaniline, of which the *platinichloride* is a red oil, and the *methiodide* a hygroscopic solid. *Methyl-p*-toluidinoacetonitrile,



prepared from methyl-*p*-toluidine by Knoevenagel's method (Abstr., 1904, i, 989), has b. p. $156-157^{\circ}/9$ mm. and m. p. 57° ; it is not acted on by cyanogen bromide. (A convenient method of preparing methyl-*p*-toluidine consists in demethylating dimethyltoluidine with cyanogen bromide. *p*-Tolylmethylcyanamide, $C_6H_4Me \cdot NMe \cdot CN$, b. p. $147^{\circ}/9$ mm., m. p. 45° , is formed together with *p*-tolyltrimethylammonium bromide, which on dry distillation gives methyl bromide and dimethyltoluidine, and the cyanamide is converted into methyl-*p*-toluidine by boiling with 30% sulphuric acid for one hour. *Benzoyl-methyl-p*-toluidine, $C_6H_4Me \cdot NMeBz$, has b. p. $198-199^{\circ}/9$ mm. and m. p. 53° .) α -Methylanilinopropionitrile, prepared by Sachs and Kraft's method (Abstr., 1903, i, 335), with the difference that the components are heated with alcohol for six instead of two hours, is also unacted on by cyanogen bromide.

When methylanilinoacetonitrile is treated with bromine in chloroform solution, a white substance separates, which is probably *p*-bromophenylmethylaminoacetonitrile hydrobromide, and this, on addition of water, gives the nitrile. Similarly, methyl-*p*-toluidinoacetonitrile furnishes *m*-bromo-*p*-tolylmethylaminoacetonitrile,



strongly refracting crystals, b. p. $161-165^{\circ}/10$ mm., m. p. 47° , which on hydrolysis yields *m*-bromodimethyl-*p*-toluidine. The latter is most conveniently prepared by brominating dimethyltoluidine, and has b. p. $243-244^{\circ}/752$ mm. (Pesci, *Gazzetta*, 1898, 28, i, 101, gives b. p. $237-238^{\circ}/744$ mm.).

The *platinichloride* forms reddish-yellow crystals, m. p. 212° (decomp.); the *picrate* has m. p. 115° . *Dimethyl-p*-toluidine *picrate* has m. p. 130° . J. C. C.

Preparation of Aromatic *o*-Nitroamino-derivatives. FURZ ULLMAN (D.R.-P. 194951).—By heating the arylsulphonyl derivatives of *o*-nitrophenol and its analogues with a primary or secondary amine, the group $O \cdot SO_2R$ is replaced by an amino-residue and a secondary or tertiary amine is produced.

o-Nitrodiphenylamine is obtained by heating a mixture of aniline, *o*-nitrophenyl *p*-toluenesulphonate, and anhydrous sodium acetate. 2:4-Dinitrodiphenylamine is produced from 3:4-dinitrophenyl benzenesulphonate and dimethylamine.

2:4-Dinitrodiphenylamine-2-carboxylic acid can be thus prepared from 2:4-dinitrophenyl *p*-toluenesulphonate and anthranilic acid.

3:5-Dinitro-4-benzylaminotoluene, $C_8H_7Me(NO_2)_2 \cdot NH \cdot CH_2 \cdot C_6H_5$, orange needles, m. p. 80° , is produced from benzylamine and 3:5-dinitro-*p*-toluenesulphonate, m. p. 152° .

4-Chloro-2:6-dinitro-1- β -naphthylaminobenzene, red needles, m. p. 201° , and 2:4-dinitro-1-naphthylphenylamine, red leaflets, m. p. 182° , can be similarly obtained from 4-chloro-2:6-dinitrophenol and β -naphthylamine and 2:4-dinitro- α -naphthol and aniline respectively by condensing the *p*-toluenesulphonates of these phenols with the appropriate amine.

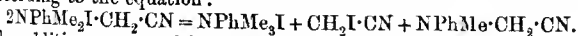
G. T. M.

Aut racemisation of Optically Active Ammonium Salts. HANS VON HALBAN (*Ber.*, 1908, 41, 2417—2421. Compare *Abstr.*, 1907, ii, 246).—Wedekind and Paschke have recently attributed (this vol., i, 334) the diminution with time of the rotatory power of optically active ammonium salts in chloroform to aut racemisation, despite the fact that the author has shown (*loc. cit.*) that it is due to the decomposition of the ammonium salt into a tertiary amine and benzyl haloid. He has therefore examined by his method the behaviour of phenylbenzylmethylallylammonium bromide in chloroform, bromoform, and tetrachloroethane at the temperatures used by Wedekind and Paschke, and has obtained, for unimolecular reactions, values of *K* which agree fairly well with those given by these investigators. In some experiments the constant increases with time. The author cannot give a cause for this, but shows that it is not due to a reaction between the liberated amine and the solvent.

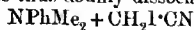
In answer to Wedekind's contention that active ammonium salts, which contain in addition to phenyl and benzyl only saturated groups, are remarkably stable in chloroform (*Abstr.*, 1907, ii, 246), the author shows that the decomposition of phenylbenzyl-diethylammonium bromide in chloroform increases with the time.

C. S.

Double Dissociation of Quaternary Ammonium Compounds and a Convenient Synthesis of Iodoacetoneitrile. JULIUS VON BRAUN (*Ber.*, 1908, 41, 2130—2144).—The reaction between bromoacetoneitrile and dimethylaniline by which phenyltrimethylammonium bromide is formed (this vol., i, 676) is explained by a study of the interaction of dimethylaniline and iodoacetoneitrile, as the latter is more reactive and a lower temperature can be employed. In this case an additive compound is first produced, which then decomposes according to the equation:

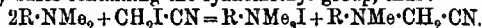


The additive compound is thus doubly dissociated into

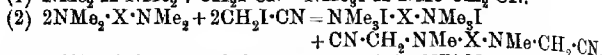
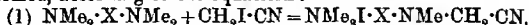


and $NPhMe \cdot CH_2 \cdot CN + CH_2I$, the first and fourth products of which at once unite. It is inferred that the analogous reaction with bromoacetoneitrile proceeds in a similar manner. As the quaternary iodide is also obtained by the action of methyl iodide on methylanilinoacetoneitrile, it is hence possible to convert half of the methyl iodide into iodoacetoneitrile, and, by employing 2 mols. of methyl iodide in the reaction, 75% of the methylanilinoacetoneitrile can be converted into iodoacetoneitrile.

The author has employed iodoacetoneitrile for the preparation of tertiary bases containing the cyanomethyl group, thus:



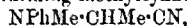
In the case of tertiary diamines, three different compounds may be formed, according to the equations:



Phenyldimethylcyanomethylammonium iodide, $NPhMe_2I \cdot CH_2 \cdot CN$, is a white, crystalline powder, m. p. 100° (decomp.). *p-Tolyl-dimethylcyanomethylammonium iodide*, m. p. 100° (decomp.), on heating yields iodoacetoneitrile, *p*-tolyltrimethylammonium iodide, and methyl-*p*-toluidinoacetoneitrile. *Phenylmethylcyanomethylethylammonium iodide*, $NPhMeEtI \cdot CH_2 \cdot CN$,

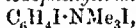
prepared from methylethylaniline and iodoacetoneitrile, is a white, crystalline powder, m. p. 100° (decomp.). On heating, it undergoes triple dissociation, giving (1) $NPhMeEt + CH_2I \cdot CN$; (2) $NPhEt \cdot CH_2 \cdot CN + MeI$, and (3) $NPhMe \cdot CH_2 \cdot CN + EtI$.

Ethylanilinoacetoneitrile and methyl iodide give phenyldimethylethylammonium iodide, m. p. 135° (Claus and Howitz, Abstr., 1884, 1005, give 126°). Methylanilinoacetoneitrile and ethyl iodide interact only slowly, with formation of a small quantity of phenylmethyldiethylammonium iodide. On warming methylethylammonium iodide,



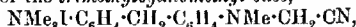
with methyl iodide, phenyltrimethylammonium iodide is produced.

By condensing iodoacetoneitrile with dimethyltoluidine and with *p*-bromodimethylaniline, methyl-*p*-toluidinoacetoneitrile and *p*-bromophenylmethyldiaminoacetoneitrile respectively are obtained much more conveniently than by the method previously described (this vol., i, 625). *p*-Iodophenylmethyldiaminoacetoneitrile, $C_6H_4I \cdot NMe \cdot CH_2 \cdot CN$, prepared from iodoacetoneitrile and *p*-iododimethylaniline, has m. p. 60° ; in the same reaction is produced *p*-iodophenyltrimethylammonium iodide,



m. p. 212° .

β -Naphthylmethyldiaminoacetoneitrile, $C_{10}H_7 \cdot NMe \cdot CH_2 \cdot CN$, prepared similarly from β -naphthylmethyldiamine, has m. p. 76° . *Thalylaminoacetoneitrile*, $OMe \cdot C_6NH_2 \cdot CH_2 \cdot CN$, prepared from methylthalline (Skraup, Abstr., 1886, 80), forms glistening crystals, m. p. 68° . When tetramethyldiaminodiphenylmethane is warmed with iodoacetoneitrile, a mixture of tetramethyldiaminodiphenylmethane dimethiodide, the methiodide of the trimethylcyanomethyl base,



m. p. $172-173^\circ$, and *biscyanomethyl-dimethyldiaminodiphenylmethane*, $CH_2(C_6H_4 \cdot NMe \cdot CH_2 \cdot CN)_2$, m. p. 107° , is produced. The latter, which is also formed by the interaction of iodoacetoneitrile and *s*-dimethyldiaminodiphenylmethane, is readily hydrolysed to the corresponding dicarboxylic acid, $CH_2(C_6H_4 \cdot NMe \cdot CH_2 \cdot CO_2H)_2$, sintering at 123° , m. p. 126° . *s*- ω -Dicyanotetramethylbenzidine is more conveniently prepared from iodoacetoneitrile and tetramethylbenzidine than by the method previously given (this vol., i, 625). When 2 mols. of dimethylaniline are warmed with 1 mol. of iodoacetophenone, there are formed phenyl

trimethylammonium iodide and methylanilinoacetophenone. No appreciable amount of the by-product obtained by Staedel and Siepermann (Abstr., 1880, 639) was formed; the author finds this to consist of *diphenacylaniline*, $\text{NPh}(\text{CH}_2\text{COPh})_2$, m. p. 225° . Dimethylaniline with iodoacetamide (m. p. 95° ; Henry, Abstr., 1885, 373, erroneously gives 157°) forms an *additive* compound, $\text{MPhMe}_2\text{I}\cdot\text{CH}_2\text{CO}\cdot\text{NH}_2$, m. p. 149° . J. C. C.

Preparation of 4-Chloro-2-aminophenol-5-sulphonic Acid. FARBEFABRIKEN FORM. FRIEDR. BAYER & Co. (D.R.-P. 194935).—On sulphonating 4-chloro-2-acetylaminophenol and hydrolysing the product, 4-chloro-2-aminophenol-6-sulphonic acid is formed, but when 4-chloro-1-hydroxybenzoxazole, $\text{C}_6\text{H}_3\text{Cl}\langle\begin{smallmatrix} \text{O} \\ \text{NH} \end{smallmatrix}\rangle\text{CO}$ or $\text{C}_6\text{H}_3\text{Cl}\langle\begin{smallmatrix} \text{O} \\ \text{N} \end{smallmatrix}\rangle\text{C}\cdot\text{OH}$, is subjected to this series of operations, 4-chloro-2-aminophenol-5-sulphonic acid is obtained. The sulphonation is effected with sulphuric acid, containing 10% of sulphur trioxide, and the hydrolysis with sodium hydroxide.

The new chloroaminophenolsulphonic acid furnishes a diazo-derivative crystallising in lustrous, yellow needles. This acid is also produced by successively sulphonating and hydrolysing 4-chloro-1-methylbenzoxazole, $\text{C}_6\text{H}_3\text{Cl}\langle\begin{smallmatrix} \text{O} \\ \text{N} \end{smallmatrix}\rangle\text{CMe}$. G. T. M.

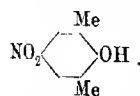
Preparation of Aromatic Hydroxylated Nitro-compounds. RICHARD WOLFFENSTEIN and O. BÖTERS (D.R.-P. 194883).—The production of a nitrophenol has hitherto necessitated the preliminary introduction of a hydroxyl group into an aromatic nucleus, a process which is often somewhat difficult. It has now been found that the hydroxylation and nitration of an aromatic hydrocarbon may be effected simultaneously by the joint action of nitric acid and mercury, or a mercury compound. A mixture of benzene (400 grams), nitric acid (660 grams, D 1.48), and mercuric nitrate (150 grams) when heated on the water-bath yields 180 grams of picric acid, together with a certain amount of nitrobenzene. A similar experiment with double quantities of nitric acid furnished picric acid (380 grams), nitrobenzene (160 grams), and 2 grams of *o*-nitrophenol.

Naphthalene treated in this way gives rise to nitronaphthols and nitronaphthalene; toluene and benzoic acid furnish respectively trinitrocresol and nitrohydroxybenzoic acid. G. T. M.

***m*-2-Xylenol.** KARL AUWERS and TH. VON MARKOVITS (Ber., 1908, 41, 2332—2340).—In connexion with their work on the oxidation of

m-2-xylenol to tetramethyldiphenquinone (Abstr., 1905, i, 219), the authors have prepared a number of new derivatives.

5-Nitro-*m*-2-xylenol, annexed formula, prepared by treating *m*-2-xylenol with nitric acid in glacial acetic acid solution, forms compact, colourless prisms, m. p. $169\text{--}170^\circ$. 5-Nitroso-*m*-2-xylenol is best obtained by acidifying a mixture of the phenol and sodium nitrite in dilute alkaline solution. It crystallises from benzene in yellow, glassy prisms and tablets, m. p. $170\text{--}171^\circ$. The *acetyl* derivative is a yellow, crystalline powder, m. p. $84\text{--}86^\circ$.



5-Bromo-*m*-2-xylénol, formed by bromination in acetic acid solution, crystallises in long, silky needles, m. p. 79.5°. 4:5-Dibromo-*m*-2-xylénol, obtained by brominating xylénol in presence of a trace of iodine or iron, forms small, colourless needles, m. p. 86—87°. By adding xylénol to excess of bromine, there is obtained 4:5:6-tribromo-*m*-2-xylénol, colourless needles, m. p. 200—201°. [The substance described under this name (Beilstein, *Handbuch*, 3rd Ed., 2, 758) is really tribromo-*p*-xylénol.] 4-Bromo-*m*-2-xylénol is prepared by brominating 2-nitro-*m*-xylene and replacing the nitro-group by hydroxyl. 4-Bromo-2-nitro-*m*-xylene, prepared by adding iron powder to a cold mixture of 2-nitro-*m*-xylene and bromine, forms shining needles, m. p. 70—71°. On reduction with zinc dust and acetic acid, diazotisation of the resulting base, and allowing the diazo-solution to decompose at the ordinary temperature, 4-bromo-*m*-2-xylénol is formed; this crystallises from light petroleum in colourless, slender needles, m. p. 60—61.5°. If steam is led into the above-mentioned diazo-solution, 4-bromo-5-nitroso-*m*-2-xylénol is obtained; this forms pale yellow needles, m. p. 190—192°. 4-Nitro-*m*-2-xylénol, prepared from 4-nitro-*m*-2-xylidino by the diazo-reaction, has m. p. 99—100°. *m*-2-Xylénol methyl ether, prepared by the use of methyl sulphate, is a colourless oil, b. p. 182°. With benzoyl chloride and aluminium chloride, it yields 4-methoxy-3:5-dimethylbenzophenone, m. p. 44°, which on warming with aluminium chloride gives 4-hydroxy-3:5-dimethylbenzophenone, colourless plates, m. p. 141—142°. 5-Benzeneazo-*m*-2-xylénol forms chrome-yellow prisms and tablets, m. p. 95—96°. J. C. C.

Phenolic Ethers containing the ψ -Allyl Side-chain -CMe:CH₂.
 III. Hydroxytoluic Series; Synthesis of Thymol. IV. Vanillic, Veratric, and Piperonylic Series. AUGUSTE DÉHAL and MARC TIFFENEAU (*Bull. Soc. chim.*, 1908, [iv], 3, 729—732, 732—738). —A continuation of work on the synthesis of these esters (this vol., i, 261). Some of the data now given have been published before (Abstr., 1904, i, 742; 1905, i, 883). 3- ψ -Allyl-*o*-cresol,

OH·C₆H₃Me·CMe:CH₂,
 D²⁰ 1.040, n_D²⁰ 1.543, b. p. 220—225°, obtained by the action of magnesium methyl iodide on methyl *o*-hydroxytoluate (m. p. 28—30°, b. p. 235°), has a characteristic thyme-like odour, gives a green coloration with ferric chloride, and with methyl sulphate yields the corresponding methyl ether, D²⁰ 0.9901, D¹⁵ 0.9830, n_D¹⁵ 1.505, b. p. 217—218°, which, on reduction with sodium in alcohol, furnishes an isothymyl methyl ether, OMe·C₆H₃Me·CHMe₂, D²⁰ 0.9589, D¹⁸ 0.9430, n_D¹⁸ 1.50725, b. p. 210—213°. The latter on demethylation with hydriodic acid gives an isothymol, D²⁰ 0.9962, b. p. 228—230°, which does not crystallise when cooled. Methyl *m*-hydroxytoluate, D²⁰ 1.1629, D²¹ 1.147, m. p. 27—28°, b. p. 118—122°/12 mm., 238—240°/760 mm., cannot be methylated by Graebe and Ullmann's process (*Ber.*, 1896, 29, 824), but with methyl sulphate or iodide gives good yields of isothymyl *m*-methoxytoluate, D²⁰ 1.1462, b. p. 259—261°/760 mm., and from the latter by the action of magnesium methyl iodide the tertiary alcohol, OMe·C₆H₃Me·CMe₂·OH, D²⁰ 1.0448, b. p. 129—136°.

11 mm., is obtained as a liquid, which, on distillation under atmospheric pressure, undergoes partial dehydration, yielding 3-methoxy-1-methyl-4- ψ -allylbenzene, D^0 0.9835, b. p. 216—219°. The latter can be prepared by heating the alcohol at 100° with acetic anhydride, a crystalline *polymeride*, D^0 1.0468, m. p. 56°, b. p. 215—223°/13 mm., being formed simultaneously. 3-Methoxy-1-methyl-4- ψ -allylbenzene on reduction with sodium in alcohol yields the methyl ether of thymol, which, on demethylation by hydriodic acid, or, better, with a mixture of hydrobromic and acetic acids, gives thymol.

Vanillyldimethylcarbinol, $\text{OMe} \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{CMe}_2 \cdot \text{OH}$
 $(\text{OMe} : \text{OH} : \text{CMe}_2 \cdot \text{OH} = 3 : 4 : 1)$,

m. p. 55°, b. p. 165°/10 mm., obtained by the action of magnesium methyl iodide on ethyl vanillate, together with a *dimeride*, m. p. 174°, of ψ -eugenol, furnishes, on distillation at atmospheric pressure, a poor yield of ψ -eugenol, $\text{OMe} \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{CMe} \cdot \text{CH}_2$ (Abstr., 1904, i, 742), m. p. 20°. The latter cannot be prepared directly by the action of magnesium methyl iodide on ethyl vanillate; it yields a crystalline benzoyl derivative, m. p. 58—59°.

Veratryldimethylcarbinol, $\text{C}_6\text{H}_3(\text{OMe})_2 \cdot \text{CMe}_2 \cdot \text{OH}$ (*loc. cit.*), m. p. 78°, b. p. 140°/7 mm., 155°/13 mm., crystallises from light petroleum, and, on distillation under atmospheric pressure, furnishes ψ -methyleugenol, $\text{C}_6\text{H}_3(\text{OMe})_2 \cdot \text{CMe} \cdot \text{CH}_2$, D^{90} 1.045, m. p. 36 (*loc. cit.*).
 ψ -Safrole (1- ψ -allyl-3:4-catecholmethylene ether), D^0 1.1338, D^{15} 1.1198, n_D^{15} 1.5619, b. p. 135°/20 mm., 233—239°/760 mm. (*loc. cit.*), obtained by the action of magnesium methyl iodide on methyl piperonylato, on reduction yields 1-isopropyl-3:4-catecholmethylene ether, D^0 1.0935, n_D^{15} 1.52315, b. p. 225—230° (Abstr., 1905, i, 883), and, on oxidation with iodine and excess of yellow mercuric oxide, piperonylacetone, $\text{CH}_2 \cdot \text{O} \cdot \text{C}_6\text{H}_3 \cdot \text{CH}_2 \cdot \text{Ac}$, D^0 1.2197, D^{22} 1.2035, n_D^{15} 1.54502, b. p. 163°/16 mm., 282—285°/760 mm. (compare Wallach, Abstr., 1904, i, 754); the *semicarbazone* of this has m. p. 159—160°. ψ -Safrole iodohydrin, on treatment with potassium hydroxide, yields an *ethylene oxide*, b. p. 150—155°/15 mm., which, on distillation under reduced pressure, yields 3:4-methylenedioxyhydratropaldehyde, b. p. 157—158°/16 mm., D^0 1.221 (compare Bougault, Abstr., 1901, i, 721); this yields a *semicarbazone*, of which the portion readily soluble in benzene has m. p. 156°, and that slightly soluble in the solvent, m. p. 158°.

T. A. H.

Derivatives of *p*-Nitrophenyl Mercaptan. EMIL FROMM and J. WITTMANN (*Ber.*, 1908, 41, 2264—2273. Compare Abstr., 1906, i, 656).—To obtain further insight into the nature of the solution of sulphur in alkali hydroxides, the action of *p*-chloronitrobenzene was studied, as this compound gives *p*-nitrophenyl mercaptan with potassium hydrosulphide (Willgerodt, Abstr., 1885, 519). The expected *p*-nitrophenylsulphoxide was, however, not obtained, but the interaction leads to the formation of sodium *p*-nitrophenoxide, 4:4'-dinitrodiphenyl disulphide (Willgerodt, *loc. cit.*), nitroamino-diphenyl sulphide (Kebmann and Baner, Abstr., 1897, i, 27), 4:4'-dinitrodiphenyl sulphide (Nietzki and Bothof, Abstr., 1895, i,

132), and the 4:4'-dinitrodiphenyl ether of *p*-azophenyl mercaptan, $N_2(C_6H_4 \cdot S \cdot C_6H_4 \cdot NO_2)_2$, m. p. 164°, which crystallises in golden-yellow needles from glacial acetic acid. Its constitution was determined by its conversion into thioaniline on reduction with tin and hydrochloric acid.

It has recently been shown that disulphides containing the group $-\ddot{O}-S-S-\ddot{O}-$ lose sulphur on treatment with alkalis, water, or amines (Abstr., 1906, *loc. cit.*), but little is known at present of the action of alkalis on aromatic disulphides. The dinitrodiphenyl disulphide gives with alcoholic sodium hydroxide the sodium salt of *p*-nitrophenyl mercaptan and an insoluble compound, $C_{24}H_{20}O_4N_2S_2$, which sinters at 130° and has m. p. 158°. As this is evidently not a direct product of the hydrolysis, the experiment was repeated with excess of benzyl chloride, when the benzyl ether of the mercaptan (m. p. 123°, Kulenkampff, *Diss.*, Freiburg, 1906) and benzoic acid were obtained. When less alkali and benzyl chloride are used, in addition to the above other, *p*-nitrobenzenesulphinato is isolated, as well as a little nitrobenzene, showing that the hydrolysis proceeds on the same lines as that of phenyl disulphido (Schiller and Otto, this Journ., 1877, i, 463). The equation $2S_2(C_6H_4 \cdot NO_2)_2 + 4KOH = 3NO_2 \cdot C_6H_4 \cdot SK + NO_2 \cdot C_6H_4 \cdot SO_2K + 2H_2O$ is held not to explain the change; the first products are supposed to be mercaptan and the hypothetical compound, $NO_2 \cdot C_6H_4 \cdot SOH$, which acts as an oxidising agent.

Dinitrodiphenyl disulphide and ammonia, when heated in a closed tube, give nitroaminodiphenyl sulphide; this compound is not formed when the corresponding monosulphide is treated in a similar manner.

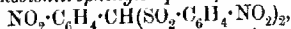
4:4'-Dinitrodiphenylsulphone, $C_{12}H_8O_4N_2S$, prepared by oxidising the sulphide with potassium dichromate and sulphuric acid, crystallises from glacial acetic acid; m. p. 282°. The corresponding diamino-derivative, $C_{12}H_{12}O_2N_2S$, forms white leaflets, m. p. 174°; its diacetate, $C_{16}H_{16}O_4N_2S$,

white needles, m. p. 280°.

p-Nitrophenylbenzylsulphone, $C_{13}H_{11}O_4NS$, has m. p. 169° (Kulenkampff, *loc. cit.*, gives 149°). When heated with methyl iodide and alcoholic sodium hydroxide, β -phenylisopropylnitrophenylsulphone, $NO_2 \cdot C_6H_4 \cdot SO_2 \cdot CPhMe_2$, is formed, m. p. 169°.

The mercaptal, $C_{15}H_{14}O_4N_2S_2$, prepared from acetone and *p*-nitrophenyl mercaptan, forms white needles, m. p. 122°. By reducing the mercaptal from benzaldehyde and *p*-nitrophenyl mercaptan (Blanksma, Abstr., 1902, i, 282), the corresponding diamino-mercaptal dihydrochloride, $C_{19}H_{20}N_2Cl_2S_2$, is obtained. The mercaptal, $C_{19}H_{18}O_4N_2S_2$, from *p*-nitrobenzaldehyde forms white needles, m. p. 166°, and on reduction gives the triamino-mercaptal trihydrochloride, $C_{19}H_{23}N_3Cl_3S_2$; the triacetate, $C_{25}H_{25}O_4N_3S_2$, has m. p. 241°.

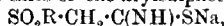
Nitrophenylmethanebisnitrophenylsulphone,



prepared from the trinitro-mercaptal by oxidation, forms light yellow leaflets, m. p. 235°. *p*-Nitrophenylthioglycine (Friedländer and Slubek, this vol., i, 525) is formed by the interaction of monochloroacetic acid and *p*-nitrophenyl mercaptan.

W. R.

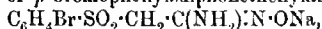
Arylsulphonated Acetonitriles. Action of Alkyl Haloids on Arylsulphon-ethenylamidoximes and -thioacetamides. JULIUS TRÖGER and BERNHARD LINDNER (*J. pr. Chem.*, 1908, [ii], 78, 1—20. Compare Abstr., 1905, i, 336).—The crystalline arylsulphonacetoneitriles, $\text{SO}_2\text{R}\cdot\text{CH}_2\cdot\text{CN}$, described by Tröger and Hille (*loc. cit.*), are sparingly soluble in water, but dissolve readily in aqueous alkalis, forming metallic derivatives analogous to those of ethyl cyanoacetate and benzyl cyanide. Tröger and Vesterling (Abstr., 1905, i, 870) found that the action of alkyl haloids on the sodioarylsulphonacetoneitriles leads to the formation of dialkyl derivatives, $\text{SO}_2\text{R}\cdot\text{CR}'_2\cdot\text{CN}$, which are even more stable towards hydrolysing agents, and form thioacetamides and amidoximes by addition of hydrogen sulphide and hydroxylamine (Tröger and Volkmer, Abstr., 1905, i, 356) with greater difficulty, than the parent nitriles. As the arylsulphonthioacetamides are readily soluble, whereas the corresponding acetamides are insoluble, in aqueous alkalis, it is considered that the thioacetamides react in the ψ -form, $\text{SO}_2\text{R}\cdot\text{CH}_2\cdot\text{C}(\text{NH})\cdot\text{SH}$; this is in agreement with the formation of benzyl sulphide by the action of benzyl chloride on the sodium salts of the arylsulphonthioacetamides,



the benzyl ether, $\text{SO}_2\text{R}\cdot\text{CH}_2\cdot\text{C}(\text{NH})\cdot\text{S}\cdot\text{CH}_2\text{Ph}$, being considered to be formed intermediately. Similarly, it is probable that the alkali salts of the amidoximes have the constitution $\text{SO}_2\text{R}\cdot\text{CH}_2\cdot\text{C}(\text{NH}_2)\cdot\text{N}\cdot\text{OM}'$. The present work was undertaken to determine in how far the arylsulphonthioacetamides and arylsulphonethenylamidoximes are capable of forming salts and ethers.

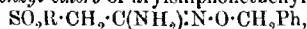
It is found that the amidoximes form stable salts only when the aryl nucleus contains a negative substituting group; if this is not the case, the alkali salt is readily hydrolysed, so that only mixtures of the salt and the free amidoxime can be obtained. The basic nature of the amidoxime group is shown by the solubility of the substances in mineral acids, and by the formation of acetyl derivatives. Whilst pure sodium salts are obtained only in certain cases, all the amidoximes studied form benzyl and methyl ethers containing the grouping $\text{N}\cdot\text{OR}$. The arylsulphonthioacetamides, on the other hand, readily form stable sodium salts, but these on treatment with benzyl chloride react, forming benzyl sulphide and not ethers of the thioacetamides.

The sodium salt of *p*-bromophenylsulphonethenylamidoxime,



forms a yellowish-red, voluminous precipitate.

The following benzyl ethers of arylsulphonethenylamidoximes,



are described. The temperatures are melting points.

$\text{R}=\text{Ph}$: white leaflets, 114° ; $\text{R}=\text{p-C}_6\text{H}_4\text{Cl}$: white needles, 114° ; $\text{R}=\text{p-C}_6\text{H}_4\text{Br}$: white needles, $132-133^\circ$; $\text{R}=\text{p-C}_6\text{H}_4\text{I}$: white needles, 165° ; $\text{R}=\text{p-C}_6\text{H}_4\text{Me}$: white prisms, 93° ; $\text{R}=\alpha\text{-C}_{10}\text{H}_7$: white leaflets, 162° ; $\text{R}=\beta\text{-C}_{10}\text{H}_7$: white leaflets, 129° ; $\text{R}=\text{o-C}_6\text{H}_4\cdot\text{OMe}$: white needles, m. p. 94° ; $\text{R}=\text{p-C}_6\text{H}_4\cdot\text{OEt}$: needles, 130° .

The methyl ethers, $\text{SO}_2\text{R}\cdot\text{CH}_2\cdot\text{C}(\text{NH}_2)\cdot\text{N}\cdot\text{OMe}$, $\text{R}=\alpha\text{-C}_{10}\text{H}_7$: white crystals, m. p. 137° , and $\text{R}=\beta\text{-C}_{10}\text{H}_7$: yellow, sandy powder, m. p. 153° (slight decomp.), were prepared.

The following *acetyl* derivatives, $\text{SO}_3\text{R}\cdot\text{CH}_2\cdot\text{C}(\text{NHAc})\text{:N}\cdot\text{OR}'$, are described.

$\text{R} = p\text{-C}_6\text{H}_4\cdot\text{OEt}$, $\text{R}' = \text{CH}_3\text{Ph}$: white needles, m. p. 115° ; $\text{R} = p\text{-C}_6\text{H}_4\text{Br}$, $\text{R}' = \text{H}$: quadratic crystals, m. p. 193° (decomp.); $\text{R} = p\text{-C}_6\text{H}_4\text{Me}$, $\text{R}' = \text{H}$: white needles, m. p. 186° .

The *sodium* salts of phenylsulphonthioacetamide, $\text{C}_6\text{H}_5\text{O}_2\text{NS}_2\text{Na}$, *p*-tolylsulphonthioacetamide, $\text{C}_9\text{H}_{10}\text{O}_2\text{NS}_2\text{Na}$, and β -naphthylsulphonthioacetamide, $\text{C}_{12}\text{H}_{10}\text{O}_2\text{NS}_2\text{Na}$, were analysed. G. Y.

Acidity of the Different Phenolsulphonic Acids. JULIUS OBERMILLER (*Zeitsch. anorg. Chem.*, 1908, 59, 79–81).—According to Ley and Erler (compare this vol., i, 177), the acidity of the phenolic hydrogen atom of phenol-*o*-sulphonic acid is weaker than that of the phenolic hydrogen of the para-acid, and this is supposed to be in agreement with Ostwald's acidity rule for aromatic dicarboxylic acids. The author points out that it is doubtful whether the para-position is further removed than the meta- from the ortho-position.

The dimagnesium salt of phenol-*o*-sulphonic acid is hydrolysed to a much smaller extent than the corresponding salt of the para-acid, and this, in opposition to Ley and Erler, indicates that phenolic hydrogen in the ortho-position is the more strongly acidic. The greater tendency of the copper salt of the ortho-acid to form basic salts cannot be explained by the weaker acidity of the acid. The author's observations on the lead salts indicate that their tendency to yield basic salts increases with increasing acidity. In respect of this property, phenol-*o*-sulphonic acid is intermediate between the para-acid and the 2:4-disulphonic acid. H. M. D.

Condensation of Nitromalonaldehyde with Acetonylacetone. I. WILLIAM J. HALE and CHARLES A. ROBERTSON (*Amer. Chem. J.*, 1908, 39, 680–696).—Hill and Hale (*Abstr.*, 1905, i, 200) have shown that the sodium derivative of nitromalonaldehyde reacts with benzyl methyl ketone with formation of 5-nitro-2-hydroxydiphenyl. It was therefore expected that nitromalonaldehyde (2 mols.) would condense with acetonylacetone (1 mol.) to form a derivative of benzyl methyl ketone, and that the latter would react with a second mol. of the aldehyde with production of a diphenyl derivative. The present paper gives an account of a study of these reactions.

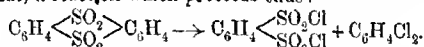
When a mixture of nitromalonaldehyde (2 mols.), acetonylacetone (1 mol.), and sodium hydroxide ($\frac{1}{2}$ mol.) was treated with carbon dioxide, a small quantity (17% of the theoretical) of 4-nitro-2-acetylphenol separated, instead of the expected diphenyl compound. On acidifying the mother liquor with hydrochloric acid, a larger quantity (about 65%) of a light yellow, crystalline substance was obtained, the description of which is reserved for a future paper.

4-Nitro-2-acetylphenol, $\text{COMe}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{OH}$, m. p. 188.5° (corr.), forms needles or prisms; its *sodium* salt crystallises with $2\text{H}_2\text{O}$. The *methyl ether* has m. p. 60° (corr.), the *ethyl ether*, 70.5° (corr.), and the *oxime*, 146° (corr.). When the methyl ether is oxidised with potassium permanganate, methyl 5-nitrosalicylate is

produced, showing that the acetonyl group is in the ortho-position to the hydroxyl group. 4:6-Dinitro-2-acetonylphenol, m. p. 121° (corr.), crystallises in lustrous plates; its *ethyl ether*, m. p. 118.5° (corr.), forms small, colourless prisms.

When 4-nitro-2-acetonylphenol is treated with nitromalonaldehyde in presence of a large excess of sodium hydroxide, 3:3'-dinitro-6:6'-dihydroxydiphenyl, $\text{NO}_2\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{NO}_2$, m. p. 391° (corr.), is produced, and crystallises in small, colourless needles. Its *dimethyl ether*, m. p. 264° (corr.), and *diethyl ether*, m. p. 271° (corr.), crystallise in needles. The *mono-ethyl ether*, m. p. 224° (corr.), obtained by the condensation of 4-nitro-2-acetonylphenyl ethyl ether with the sodium derivative of nitromalonaldehyde, forms silky needles. 3:3'-Diamino-6:6'-dihydroxydiphenyl is readily obtained by reducing the dinitro-compound with tin and hydrochloric acid; its *hydrochloride* forms long, colourless prisms. On oxidation with chromic acid, the diamino-compound is converted into diquinone, m. p. 192° (corr.) (compare Barth and Schreder, Abstr., 1885, 521). E. G.

Constitution of Thianthren [Diphenylene Disulphide]. J. J. B. DEUSS (*Ber.*, 1908, 41, 2329—2331).—The ortho-position of the sulphur atoms in diphenylene disulphide, $\text{C}_6\text{H}_4\langle\text{S}\rangle\text{C}_6\text{H}_4$ (Graebe, Abstr., 1874, 469; 1876, i, 578), has been indicated by the work of Jacobson and Ney (Abstr., 1889, 771) and of Krafft and Lyons (Abstr., 1896, i, 297), whilst Genvresse (Abstr., 1897, i, 514) considered that the sulphur atoms were in the meta-position to each other. The author has treated diphenylene disulphide with phosphorus pentachloride, a reaction which proceeds thus:



The products were benzene-*o*-disulphonyl chloride and *o*-dichlorobenzene, thus proving the ortho-position of the sulphur atoms in diphenylene disulphide. J. C. C.

Preparation of Carbamates of 2:6-Dialkyloxyphenols. BASLER CHEMISCHE FABRIK (D.R.-P. 194034).—The carbamates of the 2:6-dialkyloxyphenols (pyrogallol 1:3-dialkyl ethers) are prepared by the following series of operations: (1) condensation of carbonyl chloride with either of these ethers in the presence of a tertiary base, such as pyridine or dimethylaniline, or with sodium salts alone; (2) treatment of these intermediate products with dry ammonia.

2:6-Dimethoxyphenyl carbamate, $\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{O}\cdot\text{CO}\cdot\text{NH}_2$, is a white mass melting at 148—152°. G. T. M.

Three New Primary Alcohols Resulting from the Condensation of Sodium Benzyloxide with Propyl, Butyl, and isoAmyl Alcohols. MARCEL GUERRET (*Compt. rend.*, 1908, 146, 1405—1407).—The author has continued his work on the action of alcohols on sodium benzyloxide (this vol., i, 162). The alcohol already obtained from *n*-propyl alcohol has been proved to be γ -phenylisobutyl alcohol, $\text{CH}_2\text{Ph}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{OH}$. It is a colourless, oily liquid, b. p. 244—246°

(corr.), D_0^{20} 0.9841, with an odour recalling that of lilac. The *phenyl. carbamate* forms colourless needles, m. p. 62—63°, and the *acetate* is a colourless liquid, b. p. 260—262° (corr.). On oxidation, the alcohol gives β -phenylisobutyric acid. When sodium benzyloxide is condensed with *n*-butyl alcohol, there is formed β -benzyl-*n*-butyl alcohol, $C_6H_5 \cdot CH_2 \cdot CHEt \cdot CH_2 \cdot OH$, a colourless, oily liquid with an odour resembling that of phenylisobutyl alcohol; it has b. p. 258—261° (corr.) and D_0^{20} 0.9780. The *acetate* has b. p. 275—276° (corr.). On oxidation, the alcohol furnishes α -benzyl-*n*-butyric acid. The constitution of the benzylamyl alcohol prepared from *iso*amyl alcohol has not yet been established, but from analogy it is probably β -benzylisobutyl. *carbinol*, $CH_3Ph \cdot CH(C_3H_7) \cdot CH_2 \cdot OH$. It is a colourless, oily liquid, b. p. 272—274° (corr.), D_0^{20} 0.9687. The *acetate* has b. p. 279—281° (corr.). On oxidation, the alcohol yields *benzylvaleric acid*, $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CO_2H$, a colourless, oily liquid with an odour of valerian, b. p. 303—308° (corr.). The *potassium*, *barium*, and *silver* salts are described. The *ethyl* ester has a strong, fruity odour; it has b. p. 274—276°. The *chloride* has b. p. 156—158°/22 mm. (corr.), and the *amide* has m. p. 94—95°.

J. C. G.

Reduction with Platinum and Hydrogen. II. Dihydro cholesterol. RICHARD WILLSTÄTTER and ERWIN W. MAYER (*Ber.*, 1908, 41, 2199—2203. Compare this vol., i, 383; Windaus, *Abstr.*, 1907, i, 610).—Cholesterol is reduced when hydrogen is passed through an ethereal solution of the substance containing platinum-black in suspension, yielding dihydrocholesterol (cholestanol), $C_{27}H_{48}O$, identical with the β -cholestanol obtained by Diels and Abderhalden (*Abstr.*, 1906, i, 272) from cholestenone. This fact confirms the view of Diels and Linn (this vol., i, 164) that cholesterol and cholestenone contain the same ring complex. It follows from the values obtained for the rate of esterification of cholesterol and its dihydro-derivative that these compounds are secondary alcohols; further, as is to be expected, the absolute initial velocity of esterification of the saturated compound is greater than that of the unsaturated compound.

Dihydrocholesterol crystallises from light petroleum or acetone in prisms, m. p. 141.5—142° (corr.), and from dilute alcohol with $11H_2O$ in six-sided leaflets, which soften at 130°. The anhydrous substance in ether gives $[\alpha]_D^{22} + 28.8^\circ$. At 18°, 100 parts of alcohol dissolve 1.60 parts of cholestanol and 2.28 parts of cholesterol.

Cholestanyl acetate, $C_{29}H_{50}O_2$, obtained by acting on the alcohol with acetic anhydride, crystallises in glittering prisms, m. p. 110.5—111° (corr.).

W. H. G.

Connexion of Cholesterol and Cholic Acid with Camphor and Turpentine Oil. HUGO SCHRÖTTER and RICHARD WEITZENBÖCK (*Monatsh.*, 1908, 29, 395—398).—It was shown recently (this vol., i, 532) that, when treated with concentrated sulphuric acid and mercury and thereafter with nitric acid, cholesterol and cholic acid yield rhizocholic acid, which was considered to be hydroxycyclopentadienetricarboxylic acid. As this points to a relationship between cholesterol and cholic acid, on the one hand, and, on the other, the terpenes, which

give analogously-constituted oxidation products, it was of importance to prepare rhizocholic acid in larger quantities and to establish its constitution. It is now found that rhizocholic acid is formed in small yields when camphor and turpentine oil are treated in the same manner as cholesterol with sulphuric acid and mercury and then with nitric acid. Apart from the question as to the correctness of the constitution suggested for rhizocholic acid, these results show that cholesterol and cholic acid are genetically related to camphor and turpentine oil, and must therefore belong to the terpene group. Thus, for the first time, is demonstrated the presence of a member of the terpene group amongst the degradation products of the animal organism.

G. Y.

Ergosterol and Fongisterol. CHARLES TANRET (*Compt. rend.*, 1908, 147, 75—77).—Ergosterol is accompanied in spurred rye by a very similar crystalline substance, which also seems to exist in other fungi, and which the author designates *fongisterol*. The so-called ergosterol (Abstr., 1889, 407), having $[\alpha]_D - 114^\circ$, contains one-ninth its weight of the new compound. Separation is effected by repeated recrystallisation from ether, ergosterol being the less soluble. Pure ergosterol, $C_{27}H_{42}O_2$, is not efflorescent, and is completely dehydrated only at 105° , but the anhydrous substance quickly absorbs water from moist air. It crystallises from alcohol in wide, monoclinic lamellae, and from ether in monoclinic needles. It has m. p. 165° (on Maquenne block), $[\alpha]_D - 126^\circ$ (in chloroform), -105.5° (in ether). The acetate has $[\alpha]_D - 91.8^\circ$ and m. p. 180.5° ; the formate, $[\alpha]_D - 97.9^\circ$ and m. p. 161.5° .

Fongisterol, $C_{25}H_{40}O_2$, is a lower homologue of ergosterol; it has a similar crystalline form, and is not efflorescent. It is dehydrated by chloroform, giving a milky liquid, but, when almost anhydrous, dissolves in 10 parts of this solvent at 20° . It has m. p. 144° (on Maquenne block), $[\alpha]_D - 22.4^\circ$ (in chloroform containing 2% of alcohol), -12.9° (in ether). The acetate has m. p. 158.5° , $[\alpha]_D - 15.9^\circ$ (in chloroform), -10.8° (in ether). The reactions with sulphuric acid and chloroform and with fuming nitric acid, previously indicated to distinguish ergosterol from cholesterol, serve to differentiate the latter from fongisterol.

When a particle of fongisterol is thrown on a few drops of 90% sulphuric acid, the latter acquires a ruby-red colour in a few seconds, which, after some minutes, changes into a reddish-violet. With ergosterol, a dirty red colour only appears at the end of one minute.

Ergosterol and fongisterol seem to be widely distributed. The cholesterol described by Gerard (Abstr., 1892, 1294; 1896, i, 21; 1898, i, 549) as belonging to the ergosterol group, probably consists of a mixture of these two compounds.

E. H.

Unsaponifiable Ingredients of Cocoa-Butter and their Detection in Butter. HERMANN MATTHES and EDWIN ACKERMANN (*Ber.*, 1908, 41, 2000—2001).—The ethereal extract of cocoa-butter hydrolysed by alcoholic potassium hydroxide contains, in addition to ordinary phytosterol, a second alcohol, which gives the same colour

reactions as phytosterol, but differs from it in taking up 2 mols. of bromine and in forming a sparingly soluble *tetrabromophytosteryl acetate*, $C_{31}H_{52}O_2Br_4$, m. p. 180—183° (decomp.). As butter contains only cholesterol, which does not form a tetrabromo-acetate, the authors are studying the practical application of the reaction to the detection of cocoa-fat in butter. Other fats of vegetable and of animal origin are being examined, in the hope that the reaction will differentiate between the two classes of fats.

C. S.

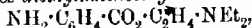
Abnormal Products of the Fission of *cyclo*Hexanecarboxylic Acid. NICOLAI D. ZELINSKY and J. GUTT (*Ber.*, 1908, 41, 2074—2076).—Whilst the corresponding hydrocarbons are readily obtained from aromatic and aliphatic acids by distillation of the calcium or barium salts with lime or soda-lime, such reactions are found in the *cyclohexane* series to be accompanied by far-reaching complications. When distilled with sodium methoxide (Mai, *Abstr.*, 1889, 1126), barium *cyclohexanecarboxylate* yields a mixture of *cyclohexadiene* with smaller amounts of *cyclohexene*, together with dihydro-toluene, whereas, when heated with zinc chloride, *cyclohexanecarboxylic acid* is converted chiefly into methyl*cyclopentane*. It is shown that Winhorn's supposed methyl*cyclohexane*, prepared by heating 1-methyl-*cyclohexane-3-carboxylic acid* with zinc chloride (*Abstr.*, 1898, i, 407), is a mixture of that substance with an isomerisation product, probably dimethyl*cyclopentane*.

G. Y.

Characteristic Reaction of Anthranilic Acid. BRONISLAW PAWLEWSKI (*Ber.*, 1908, 41, 2353—2354. Compare Suida, this vol., i, 523).—For the identification of anthranilic acid, Mohr and Köhler recommend its conversion into acetylauranil (*Abstr.*, 1907, i, 414). A still simpler method is now based on the formation of the characteristic *additive* compound of anthranilic acid and *p*-dimethylaminobenzaldehyde, $CO_2H \cdot C_6H_4 \cdot NH_2 \cdot CHO \cdot C_6H_4 \cdot NMe_2$, which is formed when the components are ground together and moistened with water or alcohol, or boiled with aqueous alcohol or benzene. If gently heated with aqueous alcohol or benzene, the acid and aldehyde form a yellow solution, which gradually deposits the red additive compound. This crystallises in needles, m. p. 180—182°, is decomposed partially on recrystallisation, or completely by ammonia, alkalis, alkali carbonates, or acids, and when treated with acetic anhydride yields *N*-acetylauranilic acid, m. p. 180—181°.

G. Y.

Preparation of Alkylaminoalkyl *p*-Aminobenzoates. FARO-WERKE VORM. MEISTER LUCIUS & BRÜNING (D.R.-P. 194748. Compare *Abstr.*, 1907, i, 923).—*Chloroethyl 4-aminobenzoate*, white needles, m. p. 86—87°, obtained either by reducing *chloroethyl 4-nitrobenzoate*, needles, m. p. 56°, or by treating 4-aminobenzoic acid with ethylene-chlorohydrin, furnishes *diethylaminoethyl 4-aminobenzoate*,



m. p. 51°, hydrochloride, m. p. 156°, on heating with diethylamine at 110°. *Chloroisopropyl 4-aminobenzoate*, needles, 69°, hydrochloride, leaflets, m. p. 186°, obtained from *chloroisopropyl 4-nitrobenzoate*, brown

oil, b. p. 195—196°/17 mm., gives rise to *piperidylisopropyl 4-aminobenzoate*, m. p. 82°, on heating with piperidine at 120°.

A similar series of esters was obtained from *p*-nitrobenzoyl chloride and α -dichlorohydrin. The final product, *dipiperidylpropyl 4-aminobenzoate*, forms prismatic plates, m. p. 158°. G. T. M.

Preparation of Dialkylaminoalkyl Diaminobenzoates.
ALFRED EINHORN (D.R.-P. 194365).—*Diethylaminoethyl 3:4-diaminobenzoate*, $C_6H_3(NH_2)_2 \cdot CO_2 \cdot C_2H_5 \cdot NEt_2$, oil, *hydrochloride*, needles, m. p. 163°, may be prepared from 3:4-diaminobenzoic or 3-nitro-4-aminobenzoic acid by the following alternative series of operations. The former of these acids, or its methyl ester, is either treated with diethylaminomethylcarbinol, $CH_2(NEt_2) \cdot CH_2 \cdot OH$, or condensed successively with ethylene chlorohydrin and diethylamine. The intermediate *chloroethyl 3:4-diaminobenzoate* crystallises from benzene and petroleum in needles, m. p. 80°. The latter acid is condensed with ethylenechlorohydrin to *chloroethyl 3-nitro-4-aminobenzoate*, brownish-yellow needles or plates, m. p. 145—146°. Diethylamine converts this ester into *diethylaminoethyl 3-nitro-4-aminobenzoate*,

$NO_2 \cdot C_6H_3(NH_2) \cdot CO_2 \cdot C_2H_5 \cdot NEt_2$,
yellow oil, *hydrochloride*, yellow needles, m. p. 208°, and this product, on reduction with tin and hydrochloric acid, furnishes the required ester of diaminobenzoic acid.

Diethylaminoethyl 3-amino-4-dimethylaminobenzoate,
 $NMe_2 \cdot C_6H_3(NH_2) \cdot CO_2 \cdot C_2H_5 \cdot NEt_2$,
oil, *hydrochloride*, needles, m. p. 164°, is derived by a similar series of operations from 3-nitro-4-dimethylaminobenzoic acid. These products are valuable anaesthetics of the novocaine series. G. T. M.

Optical Resolution of Aminophenylacetic Acid. MARIO BETTI and MARIO MAYER (*Ber.*, 1908, 41, 2071—2073. Compare Abstr., 1907, i, 726; Ehrlich, this vol., i, 268; Fischer and Weichhold, *ibid.*, 419).— α -Aminophenylacetic acid has been resolved into its optically active constituents by means of *d*-camphorsulphonic acid and *d*-bromocamphorsulphonic acid.

l- α -Aminophenylacetic acid *d*-camphorsulphonate, $C_{18}H_{25}O_6NS$, separates from an aqueous solution of the two acids in colourless, trimetric, strongly refracting crystals, m. p. 210—212° (decomp.), $[\alpha]_D - 44.07^\circ$, and, on treatment with an alkali, yields *l*- α -aminophenylacetic acid, m. p. above 305°, $[\alpha]_D - 111.02^\circ$. *d*- α -Aminophenylacetic acid, obtained from the mother liquors, has $[\alpha]_D + 112.18^\circ$.

d- α -Aminophenylacetic acid *d*-bromocamphorsulphonate,
 $C_{18}H_{24}O_6NSBr \cdot 3H_2O$,
separates from water as a crystalline mass, and loses $3H_2O$ at 65°, m. p. 200—210° (decomp.), $[\alpha]_D + 85.94^\circ$. The *d*- α -aminophenylacetic acid obtained from this has $[\alpha]_D + 110.60^\circ$. The *l*- α -aminophenylacetic acid obtained from the mother liquors has $[\alpha]_D - 107.20^\circ$.

Attempts to resolve aminophenylacetic acid by means of bornylamine were unsuccessful, as stable salts are not formed. G. Y.

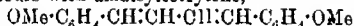
Oxidation of *allo*-Cinnamic Acid. C. N. RIEBER (*Ber.*, 1908, 41, 2411—2416).—The author confirms Fittig and Rür's statement that

careful oxidation of cinnamic acid by dilute potassium permanganate yields the phenylglyceric acid, m. p. 141° (Abstr., 1892, 986), but considers it highly improbable that the substance obtained by Michael from *allo*-cinnamic acid in a similar manner and claimed by him to be the phenylglyceric acid, m. p. 121° (Abstr., 1902, i, 32), can in reality be such, since the method of isolation and the properties of the substance indicate that Michael was dealing with benzoic acid. A repetition of Michael's experiment has resulted in the isolation only of benzoic and oxalic acids.

Phenylglyceric acid, m. p. 121° , is obtained, however, when *methyl allo*-cinnamate, b. p. $49^{\circ}/0.1$ mm., prepared from the silver salt and methyl iodide, is oxidised in alcoholic alkaline solution at -15° to -17° by 0.5% potassium permanganate. C. S.

Liquid Crystals. TH. ROTARSKI (*Ber.*, 1908, 41, 1994—1998).—The following substances are mentioned which form liquid crystals concerning which no statement is to be found in the literature of anisotropic liquids.

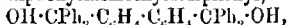
The anisotropic liquid phase of *p*-methoxycinnamic acid must be conditioned by the group $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot$, since the same phenomenon occurs with dianisyltetraphenylene,



(Fittig and Politis, Abstr. 1890, 770). Several investigators have prepared *p*-methoxycinnamic acid without mentioning the anisotropic character of the liquid form. The substance prepared by Perkin's method has m. p. 170° , the turbid liquid clarifying at 185° . After being heated ten times to 200° , the acid melts at 158° to a clear liquid, but, after purification, again shows its original m. p. and clarifying point (169° and 186° respectively). The ebullioscopic method indicates that *p*-methoxycinnamic acid in nitrobenzene exists in the bimolecular form; in this connexion it is worthy of note that the acid remains unchanged under conditions such as precipitation by water from its solution in cold concentrated sulphuric acid, distillation under ordinary pressure, and deposition by prolonged evaporation in sunlight of its solution in benzene, under which the various forms of unimolecular cinnamic acid and its polymericides, α - and β -truxillic acids, undergo conversion one into another. *p*-Methoxycinnamic acid is not affected by six hours' heating with water or 20% sodium hydroxide at 175 — 180° .

p-Methylaminobenzaldehydephenylhydrazine melts at 170° to a turbid liquid, which becomes clear at 190° ; the corresponding ethyl derivative has 160° and 182° respectively (*Chem. Zentr.*, 1900, i, 1114). *s*-Diethylbenzidine has m. p. 115.5° , the milky liquid clearing at 120.5° (Hofman, *Annalen*, 1860, 115, 365; Tichwinski, Abstr., 1904, i, 267).

The cases of 4:4'-diphenylbismethyldiphenyl,



m. p. 160° , clarifying point 186° , and its chloride, m. p. 219° , clarifying point 223° , have not been settled, since the author could not prepare the compounds, and the discoverer, Tschitschibahin (Abstr., 1907, i, 503), could not give a definite opinion.

p-Methoxycinnamaldehyde, $N_2[CH:OH:CH \cdot O_6H_4 \cdot OMe]_3$, obtained from *p*-methoxycinnamaldehyde and hydrazine sulphate in alkaline solution, separates from benzene in yellow crystals and gives a purple-red coloration with concentrated sulphuric acid. It melts at 210° and clarifies at 218° , but, owing to decomposition, the substance resolidifies without becoming turbid. C. S.

Clear, Transparent, Crystalline Liquids. DANIEL VORLÄNDER (*Ber.*, 1908, 41, 2033—2052).—The view that the optical properties of turbid, crystalline liquids are merely due to suspensions or emulsions is rendered untenable, as it is now shown that perfectly clear, transparent liquids can exhibit similar optical properties, for example, double refraction. Such liquids behave exactly like a thin section of quartz or calcite cut at right angles to the principal axis.

The relationship between constitution and capacity for producing liquid crystals has been further examined (compare Abstr., 1906, i, 317, 1907, ii, 337, 442) by the inclusion of a number of substituted benzylidenes-amino- α -alkylated cinnamic esters, obtained by condensing the esters of α -substituted cinnamic acids with anisaldehyde, *p*-ethoxybenzaldehyde, and *p*-phenylbenzaldehyde.

[With W. KASTEN.]—The following esters have been examined; Methyl *p*-methoxybenzylidenes-amino- α -methylcinnamate, monotropic, crystalline liquid, but indication of 2 crystalline liquid phases when sufficiently cooled, m. p. 133° ; ethyl ester, 1 enantiotrop. liq. cryst. phase, 2 solid phases, m. p. 89° and 93° ; *n*-propyl ester, enantiotrop. cryst. liq., 2 m. p., 50° and 85° ; *n*-butyl ester, monotrop., m. p. 58° ; isocamyl ester, monotrop., m. p. $46-47^\circ$; active amyl ester, 2 or 3 cryst. liq. phases, 1 enantiotrop. and 2 strongly circularly polarising, m. p. $60-68^\circ$.

Ethyl *p*-methoxybenzylidenes-amino- α -ethylcinnamate shows little tendency to form a crystalline liquid, and has m. p. $60-61^\circ$; the active amyl ester has not been obtained crystalline.

Ethyl *p*-methoxybenzylidenes-amino- α -phenylcinnamate does not form a crystalline liquid, and has m. p. 108° .

Methyl *p*-ethoxybenzylidenes-amino- α -methylcinnamate, 1 enantiotrop. cryst. liq. and 1 monotrop. cryst. liq. phase, 2 solid phases, m. p. 105° and 147° ; ethyl ester, 1 enantiotrop. and 1 monotrop. cryst. liq. phase, both pseudoisotropic, 2 solid phases, indications of a third cryst. liq. phase, transition temperatures 124° , 94° , and 76° ; *n*-propyl ester, 1 enantiotrop. and 1 monotrop. cryst. liq. phase, both pseudoisotropic, m. p. 88° and 121° ; *n*-butyl ester, 2 cryst. liq. phases, enantiotrop.; m. p. 55° , 65° , and 82° ; isocamyl ester, enantiotrop. cryst. liq., m. p. 83° and 90° ; active amyl ester, 3 cryst. liq. phases, 2 enantiotrop. m. p. 86° and 100° .

Ethyl *p*-ethoxybenzylidenes-amino- α -ethylcinnamate, 2 monotrop. cryst. liq. phases, both pseudoisotropic, 2 solid phases, transition temperatures 73° , 61° , and 45° ; *n*-propyl ester, monotrop. cryst. liq., m. p. 98° and 63° ; active amyl ester, 3 cryst. liq. phases, 2 strongly circularly polarising, m. p. 69° .

Ethyl *p*-ethoxybenzylidenes-amino- α -isopropylcinnamate, scarcely crystalline liquid, m. p. $76-77^\circ$.

Ethyl *p*-phenylbenzylidenes-amino- α -cinnamate, 4 cryst. liq. phases, all

enantiotrop., and under certain conditions pseudoisotropic, 1 in needles and 1 in rods, transition temperatures 216° , 207° , 204° , 178° , and 145° ; *n*-butyl ester, 2 cryst. liq. phases, enantiotrop., m. p. 167° and 203° , liquid crystals from aqueous acetone; isoamyl ester, 2 cryst. liq. phases, enantiotrop., m. p. 164° , 188° , and 197° , liquid crystals from light petroleum; active amyl ester, 2 cryst. liq. phases, enantiotrop., m. p. 115° , 153° , and 180° .

Ethyl p-phenylbenzylideneamino- α -methylcinnamate, 3 cryst. liq. phases, all enantiotrop. and pseudoisotrop., m. p. 120° , 148° , and 173° ; *n*-butyl ester, 2 or 3 liq. cryst. phases, enantiotrop., m. p. 100° , 136° , and 148° ; active amyl ester, crystalline resin from aqueous acetone.

Ethyl phenylbenzylideneamino- α -ethyl cinnamate, 2 cryst. liq. phases, monotrop. and pseudoisotrop., 2 solid phases, m. p. 139° ; *n*-propyl ester, 1 enantiotrop. cryst. liq. and 1 monotrop. cryst. liq. phase, both pseudoisotropic, m. p. 118° and 135° ; active amyl ester, crystalline resin, clarifies at 118° .

Ethyl p-azocinnamate, 2 enantiotrop. cryst. liq. phases, m. p. 155 – 230° , at least 3 solid phases. *Ethyl p*-azo- α -methylcinnamate, monotrop. cryst. liq., m. p. 112° , 2 solid phases. *Ethyl p*-azoxy-cinnamate, enantiotrop. cryst. liq., m. p. 141° and 250° .

Ethyl p-azoxy- α -methylcinnamate, 2 or 3 enantiomorp. cryst. liq. phases, 3 or 4 solid phases, m. p. between 110° and 140° . *Ethyl β* -bromo-*p*-azoxy- α -methylcinnamate, 2 pseudoisotrop. cryst. liq. phases, m. p. 110° . *Ethyl p*-azoxy- α -ethylcinnamate, m. p. 85° , scarcely crystalline liquid, and *ethyl p*-azoxy- α -phenylcinnamate, m. p. 154° , scarcely crystalline liquid.

The following general conclusions are drawn:

1. With the lengthening of the alkyl radicle of the CO_2R group, the tendency to form liquid crystals attains a maximum usually at the ethyl or *n*-propyl ester.
2. The radicles methoxyl, ethoxyl, and phenyl in the para-position strengthen the tendency to form liquid crystals; ethoxyl and phenyl have much the same effect, and this is greater than with methoxyl.
3. The tendency for liquid crystal formation is lessened by the introduction of alkyl groups in the α -position and in the order methyl, ethyl, phenyl.
4. The introduction of the optically active amyl radicle converts the crystalline liquid into a strongly circularly polarising condition.

The effect of β -substituents will be studied later. The rotation of some of the amyl esters is enormous. A mixture of amyl anisylideneaminocinnamate and amyl anisylideneamino- α -methylcinnamate in the crystalline liquid state has a rotatory power $+5300^{\circ}$ for sodium light and for a layer 1 mm. thick.

The molecules of the crystalline liquid may be regarded as arranging themselves in wavy rods, in long straight rods, or in short rods at right angles to the plates on which the drops are placed. In the last case, the pseudoisotropic form of Lehmann is obtained. Many of the new esters examined have this form, and are perfectly clear. Frequently when a turbid, crystalline liquid is rubbed with a needle or is pressed between glass plates, it becomes clear, and it is thus possible at will to obtain the clear or turbid, crystalline liquid condition.

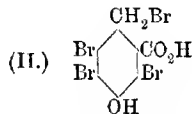
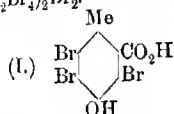
Certain esters appear clear when examined in any position; others,

for example, ethyl and active amyl anisylideneaminocinnamate, are clear when examined in light which falls at right angles, but turbid when examined in reflected light or light at any other angle.

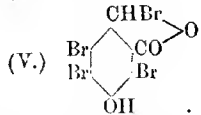
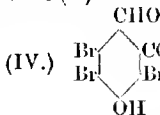
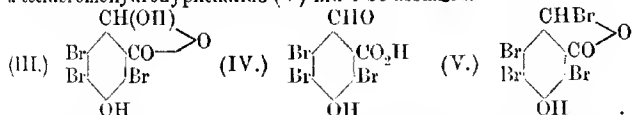
The crystalline liquids have been examined in many cases with the aid of the ultra-microscope, and also in converging polarised light. The result of the latter examination is to prove the uniaxial nature of the liquid crystals.

Measurements of the double refraction of many of the liquids have been made; the clear liquid esters of α -alkylated cinnamic acids are about twice as strongly refractive as calcite. J. J. S.

Hydroxytoluic Acids. II. 4-Hydroxy-*o*-toluic Acid. THEODOR ZINCKE and M. BUFF (*Annalen*, 1908, 361, 218—250).—It was shown previously (Abstr., 1907, i, 132) that 4-hydroxy-*o*-toluic acid forms a tribromo- (I) and a tetrabromo- (II) derivative and a perbromide, $(C_8H_4O_2Br_4)_2Br_2$.

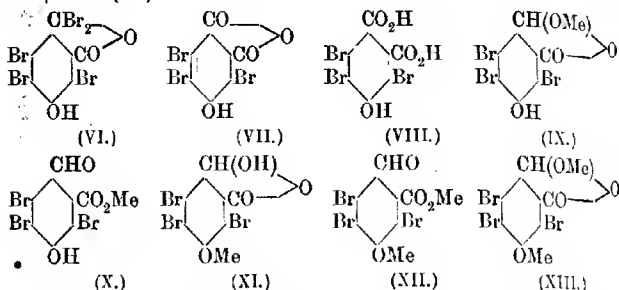


The action of an excess of bromine on the tribromo-derivative led to the formation of a mixture of compounds which could not then be separated. In some experiments, compounds were obtained which contained a smaller amount of bromine than the parent substance, and gave an intense yellow coloration with sodium carbonate. This led the authors to continue the investigation. It is now found that, in addition to the tetrabromo-acid and the perbromide, four new compounds are formed by the action of bromine on the tribromo-acid, the nature of the product depending, not on the excess of bromine, but on the presence or absence of moisture and on the temperature. In absence of moisture, the action of bromine on the tribromo-acid at 130—140° leads to the formation of the tetrabromo-acid and the perbromide, whilst at higher temperatures the product resinifies; but with a limited amount of moist bromine at 130—140°, the tribromo-acid yields a tribromohydroxyphthalide (III) or tribromoaldehyde-acid (IV). The intermediate formation of the tetrabromo-acid and of a tetrabromohydroxyphthalide (V) must be assumed.



Under certain conditions, a pentabromo-derivative (VI) is formed, which is converted by water into tribromo-4-hydroxyphthalic anhydride (VII); this is the chief product when slightly more moist bromine is employed for bromination of the tribromo-acid. The pentabromo-derivative (VI) is readily obtained by the action of bromine on tribromo-4-hydroxyphthalide (III) at 180—185°. Tribromo-4-hydroxyphthalic acid (VIII) is readily obtained from the pentabromo-compound (VI) or the tribromohydroxyphthalic anhydride (VII).

Tribromo-4-hydroxyphthalide (III) yields a diacetyl derivative and ψ -methyl ester (IX). A normal ester (X) corresponding to this could not be obtained; the silver salt forms with methyl iodide the methyl ether (XI). The silver salt of this ether gives rise to a normal ester (XII) and a ψ -ester (XIII), which is formed also from the ψ -ester (IX).



Tetrabromo-4-hydroxyphthalide (V) could not be obtained free from the aldehyde-acid; the mixture forms crystalline aggregates, m. p. 196°, and, when heated with methyl alcohol and sulphuric acid, yields the ψ -methyl ester of the aldehyde-acid.

The tribromo-4-hydroxyaldehyde-acid, (III) or (IV), crystallises from tetrachloroethane in colourless needles, m. p. 238° (decomp.), and, when heated with bromine at 170—175°, yields tribromo-4-hydroxyphthalic anhydride. The diacetyl derivative, $\text{OAc} \cdot \text{C}_6\text{Br}_3 \cdot \text{CH}(\text{OAc}) \cdot \text{CO}$, formed by the action of acetic anhydride and sulphuric acid on the aldehyde-acid, crystallises in white leaflets, m. p. 177—178°. The ψ -methyl ester (IX), prepared by heating the aldehyde-acid with methyl alcohol and sulphuric acid, forms needles, m. p. 232—233°, gives an intense yellow coloration when heated with phenylhydrazine in acetic acid, but crystallises unchanged on cooling, and forms an acetyl derivative $\text{C}_{11}\text{H}_7\text{O}_5\text{Br}_3$, needles, m. p. 179—180°.

The ψ -dimethyl ester (XIII), formed by the action of methyl iodide on the silver salt of the ψ -monomethyl ester, or by boiling the corresponding normal ester with methyl alcohol, crystallises in white needles, m. p. 184—185°, gives a yellow coloration when heated with phenylhydrazine in acetic acid, forms the acetyl derivative of the methyl ether when heated with acetic anhydride and sulphuric acid, and is hydrolysed with sodium hydroxide, forming the methyl ether.

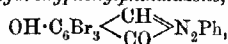
The normal dimethyl ester (XII) crystallises from benzene-light petroleum in prisms, m. p. 140—141°, and forms a phenylhydrazine derivative, $\text{OMe} \cdot \text{C}_6\text{Br}_3(\text{CO}_2\text{Me}) \cdot \text{CH} \cdot \text{N}_2\text{HPh}$, which crystallises in yellow needles, m. p. 166—167°.

The methyl ether (XI), formed by the action of methyl iodide on the silver salt of the aldehyde-acid, or by hydrolysis of the two dimethyl esters, crystallises from benzene in leaflets, m. p. 202—203°, or from dilute methyl alcohol in needles, m. p. 216—218°, and forms an acetyl derivative, $\text{C}_{11}\text{H}_7\text{O}_5\text{Br}_3$, prisms, m. p. 188—189°. With phenyl

hydrazine it forms a *derivative*, $\text{OMe} \cdot \text{C}_6\text{Br}_3 \left\langle \begin{smallmatrix} \text{CH:N} \\ \text{CO:NPh} \end{smallmatrix} \right\rangle$, crystallising in colourless needles, m. p. 240—242° (decomp.).

With aniline in hot glacial acetic acid solution, the aldehydo-acid forms an *anilide*, $\text{OH} \cdot \text{C}_6\text{Br}_3(\text{CO}_2\text{H}) \cdot \text{CH:NPh}$, which crystallises in white needles, decomp. above 200°; this forms yellow salts, which are considered to have a quinonoid constitution. The alkali salts are decomposed by water, and form colourless solutions; the *aniline salt*, $\text{O} \cdot \text{C}_6\text{Br}_3(\text{CH:NHPh}) \cdot \text{CO}_2\text{H} \cdot \text{NH}_4\text{Ph}$, forms a yellow, crystalline mass, and is decomposed by alkalis with formation of aniline.

3:5:6-Tribromo-4-hydroxyphenylphthalazone,



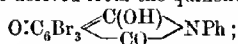
formed from the aldehydo-acid and phenylhydrazine in glacial acetic acid solution, crystallises in white needles, m. p. 224—225°. The acetyl derivative, $\text{C}_{16}\text{H}_5\text{O}_3\text{N}_2\text{Br}_3$, white needles, m. p. 171°.

The *pentabromo-4-hydroxyphthalide* (VI) crystallises from benzene-light petroleum in white leaflets, m. p. 178—179°, and on hydrolysis with alkalis yields tribromo-4-hydroxyphthalic acid. The *acetyl derivative*, $\text{C}_{10}\text{H}_3\text{O}_4\text{Br}_3$, white needles, m. p. 158°. The action of methyl alcohol, aniline, and phenylhydrazine leads to the formation of the derivatives of the tribromo-anhydride.

3:5:6-Tribromo-4-hydroxyphthalic anhydride (VII) is the final product of the action of moist bromine on tribromo-4-hydroxy-*o*-toluic acid, and is formed also by the action of moist bromine on tribromo-4-hydroxyphthalide, or of dry bromine on tribromo-4-hydroxyaldehydo-phthalic acid; it crystallises in stout prisms, m. p. 220°, dissolves in acetone or alcohol, forming a slightly yellow solution with fluorescence when dilute, and is slowly hydrolysed by boiling water, forming the corresponding acid. The anhydride forms yellow *alkali* and *aniline*, $\text{C}_{11}\text{H}_3\text{O}_4\text{NBr}_3$, salts, which are considered to have a quinonoid structure; the *pyridine salt*, $\text{C}_{13}\text{H}_6\text{O}_4\text{NBr}_3$, forms yellow crystals, m. p. 215—216°. The *acetyl derivative*, $\text{C}_{10}\text{H}_3\text{O}_5\text{Br}_3$, crystallises in white needles, m. p. 226°.

3:5:6-Tribromo-4-hydroxyphthalanil, $\text{OH} \cdot \text{C}_6\text{Br}_3 \left\langle \begin{smallmatrix} \text{C(NPh)} \\ \text{CO} \end{smallmatrix} \right\rangle \text{O}$ or

$\text{OH} \cdot \text{C}_6\text{Br}_3 \left\langle \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} \right\rangle \text{NPh}$, formed by the action of aniline on the pentabromo- or tribromo-4-hydroxyphthalic anhydride in glacial acetic acid solution, crystallises in yellow needles, m. p. 247—248°, and forms yellow salts, which are derived from the quinonoid form,



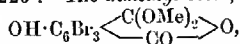
the *aniline salt*, m. p. 182—183°. The *acetyl derivative* of the anil, white needles, m. p. 224—225°. *Tribromo-4-hydroxyphthalanilic acid*, $\text{OH} \cdot \text{C}_6\text{Br}_3(\text{CO}_2\text{H}) \cdot \text{CO} \cdot \text{NHPh}$, formed by boiling the phthalanil with alkalis, is obtained as a white, crystalline powder, m. p. 110—120°, and after resolidification, 240°. The *phenylhydrazone* of tribromo-4-hydroxyphthalic anhydride, $\text{OH} \cdot \text{C}_6\text{Br}_3 \left\langle \begin{smallmatrix} \text{C(N}_2\text{HPh)} \\ \text{CO} \end{smallmatrix} \right\rangle \text{O}$, crystallises in yellow needles, m. p. 265—266° (decomp.), and with alkalis gives

a yellow coloration and then a colourless solution, which becomes violet and gives a white precipitate with acids.

3:5:6-Tribromo-4-hydroxyphthalic acid, $C_6H_3O_5Br_3$, crystallises in white needles, m. p. 220° , after sintering at 100° , and forms colourless salts with alkalis and aromatic bases. The methyl hydrogen ester,

$OH \cdot C_6Br_3 \begin{smallmatrix} C(OH)(OMe) \\ \diagup \quad \diagdown \\ CO \end{smallmatrix} O$, is formed by the action of a limited

amount of methyl alcohol and concentrated sulphuric acid on the anhydride; it crystallises in white needles, m. p. $130-140^\circ$, and after resolidification, 220° . The dimethyl ester,



is prepared by the action of methyl iodide on the silver salt of the acid or of the methyl hydrogen ester, or of methyl alcohol on the pentabromo-anhydride; it crystallises in prisms, m. p. 148° , dissolves in alkalis, forming colourless solutions, and yields an acetyl derivative crystallising in leaflets, m. p. 124° .

G. Y.

Combination of Benzoic Acid with Amines. HANS VON LIMBIG (*J. pr. Chem.*, 1908, [ii], 78, 47-48).—When fused together, benzoic acid and phenols combine to form tritanic acids (this vol., i, 445, 540); in the same manner, benzoic acid combines with amines at $180-200^\circ$, the reaction leading at least in part to the formation of compounds of high molecular weight. Aniline and benzoic acid form a compound, $C_{60}H_{49}O_3N_3$, which crystallises from benzene in needles, m. p. 176° , is insoluble in aqueous sodium carbonate, and gives with concentrated sulphuric acid a brownish-red coloration rapidly becoming yellowish-brown. The composition of this product is that of 3 mols. of aminotritanic acid less 1 mol. of water.

Benzoic acid and *o*-toluidine form three products, which are insoluble in aqueous sodium carbonate:

(a) $C_{68}H_{55}O_3N_3$, crystallises in needles, m. p. 185° , is readily soluble in alcohol, gives a violet-brown coloration with concentrated sulphuric acid, and corresponds to the compound obtained from aniline.

(b) $C_{68}H_{48}O_3N_3$, crystallises in needles, m. p. 208° , is soluble in boiling alcohol, gives a lemon-yellow coloration with sulphuric acid, and in its composition is equivalent to 3 mols. of aminomethyltritanic acid less 3 mols. of water and 1 mol. of ammonia.

(c) The lactam of 2-amino-3-methyltritanic acid,



crystallises in needles, m. p. 278° , is insoluble in boiling alcohol, and gives a weak yellow coloration with sulphuric acid.

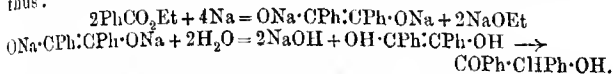
G. Y.

Preparation of Anthroxanic Acid. KALLE & Co. (D.R.P. 195812. Compare this vol., i, 421).—*o*-Nitromandelic acid or its salts are readily reduced by zinc dust and water even in the absence of ammonium chloride.

The aqueous solution when acidified after reduction yields the

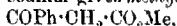
compound (nitrosomandelic acid?) melting at 130—135°; this product when treated with an alkali hydroxide passes into an alkali anthroxanate, which furnishes crystalline anthroxanic acid on treatment with acid. The reduction may be effected with other metals, providing that a temperature of 75° is not exceeded. G. T. M.

Preparation of Benzoylacetic Esters. ANDRÉ WAHL (*Compt. rend.*, 1908, 147, 72—74).—Lœwig and Werdurann (*Ann. Phys. Chem.*, 1855, 50, 95), by the action of sodium on cold ethyl benzoate, obtained a badly-defined, brown, resinous substance, which they called "hypobenzoylous acid." From this product the author has isolated benzoin, which is probably formed by reactions similar to those observed by Bonveault and Locquin (*Abstr.*, 1905, i, 560) with aliphatic esters, thus:



Accordingly, addition of sodium to a mixture of ethyl acetate and benzoate may give rise to three reactions: (1) the action of sodium on ethyl acetate, giving ethyl acetoacetate; (2) that of sodium on ethyl benzoate, giving benzoin, and (3) that of the metal on the mixture of esters, producing ethyl benzoylacetic. In order that the last reaction shall predominate, it is necessary that the ethyl benzoate shall not come into contact with excess of sodium, whilst the latter must not meet with excess of ethyl acetate. Under these conditions, the yield is better than that obtained by Claisen and Lowman (*Abstr.*, 1887, 583).

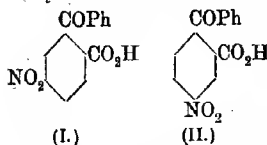
[With YOSHISAKA.]—Condensation of methyl benzoate with methyl acetate in the presence of sodium gives *methyl benzoylacetic*,



an amber-coloured liquid, b. p. 152°/15 mm., D_4^{20} 1.173, which forms a copper salt as a yellowish-green, crystalline powder, m. p. 200—201°. *Methyl nitrosobenzoylacetic* forms colourless prisms, m. p. 140°; *methyl benzeneazobenzoylacetic*, yellow prisms, m. p. 76°; *methyl p-nitrobenzeneazobenzoylacetic* crystallises in yellow spangles, m. p. 148—149°; the corresponding acid, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}(\text{H})\cdot\text{N}:\text{C}(\text{CO}_2\text{H})\cdot\text{COPh}$, forms yellow needles, m. p. 225—226° (decomp.). As in the case of the acetylacetic esters (Peters, *Abstr.*, 1890, 1096), higher esters of benzoylacetic acid can be prepared from the methyl derivative by simple displacement. Thus, when methyl benzoylacetic is boiled with excess of *isobutyl* alcohol, *isobutyl benzoylacetic*, a light yellow liquid, b. p. 160°/12 mm., is formed. E. H.

m-Nitro-o-benzoylbenzoic Acid. JOSEF RAINER (*Monatsh.*, 1908, 29, 431—437).—The condensation of 4-nitrophthalic anhydride with benzene in presence of aluminium chloride was found to lead to the formation of two nitrobenzoylbenzoic acids (this vol., i, 539), one of which is identical with Kliegl's acid (*Abstr.*, 1905, i, 187),

and is therefore 4-nitro-2-benzoylbenzoic acid (I). The isomeride,



which is formed in the larger amount, must be 5-nitro-2-benzoylbenzoic acid (II).

5-Nitro-2-benzoylbenzoic acid crystallises from methyl alcohol in quadratic leaflets containing CH_3O , or from water in needles, m. p. 212° . The silver salt, $\text{C}_{14}\text{H}_8\text{O}_5\text{Na}$, was analysed. The methyl ester, prepared by boiling the acid with methyl alcohol and sulphuric acid, crystallises in hexagonal prisms, m. p. $123.5-124^\circ$, and gives only a faint yellow coloration with concentrated sulphuric acid. The isomeric *o*-ester (compare Goldschmiedt and Lipschütz, Abstr., 1904, i, 168; 1905, i, 132; Meyer, Abstr., 1904, i, 747; 1905, i, 133), obtained by converting the acid into its chloride by means of thionyl chloride and treating the product with methyl alcohol in chloroform solution, has m. p. $104-105^\circ$, and gives an intense, yellow coloration with concentrated sulphuric acid. When heated with concentrated sulphuric acid, 5-nitro-2-benzoylbenzoic acid condenses to 2-nitroanthraquinone (Kliegl, loc. cit.).

5-Amino-2-benzoylbenzoic acid, $\text{C}_{14}\text{H}_{11}\text{O}_3\text{N}$, formed by reduction of the nitro-acid with ferrous sulphate and ammonia, crystallises in yellow, rhombic needles, m. p. $193-194^\circ$ (decomp.), or $195-196^\circ$ in a sealed capillary tube, and forms a crystalline silver salt. G. Y.

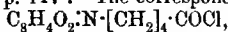
Preparation of Acylbenzoic Acids from Phthalic Anhydride, Hydrocarbons, and Aluminium Chloride. GUSTAV HELLER (D.R.-P. 193961).—The higher hydrocarbons, such as naphthalene or anthracene, do not readily condense with phthalic anhydride in the presence of aluminium chloride, but when allowed to react in the presence of benzene, toluene, or xylene, an excellent yield of naphthylbenzoic or anthracylbenzoic acid is obtained. The reaction goes in this sense when the calculated amount of higher hydrocarbon is employed, even although the benzenoid hydrocarbon may be in excess. Apparently, naphthalene or anthracene displaces benzene in the additive compound produced from the latter hydrocarbon with phthalic anhydride and aluminium chloride. G. T. M.

Preparation of Methylthiosalicylic {*o*-Methylthiolbenzoic} Acid. FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 193800).—By treating sodium dithiosalicylate with methyl sulphate in methyl-alcoholic solution, a poor yield of methyl *o*-methylthiolbenzoate is obtained, but on boiling an alkaline solution of the dithio-acid with sodium methyl sulphate, the reaction only goes as far as the production of the monomethyl derivative. The addition of dilute acid to the solution sets free *o*-methylthiolbenzoic acid, $\text{SMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, b. p. $168-169^\circ$. G. T. M.

δ -Aminoketone Derivatives. SIEGMUND GABRIEL (Ber., 1908, 41, 2010-2014. Compare this vol., i, 464, and following abstract).— α - and β -Aminoketones are fairly stable, whereas γ -aminoketones readily lose water, yielding phenylpyrroline derivatives. It is now

shown that δ -aminoketones are also unstable and readily yield anhydro-derivatives.

δ -Phthaliminovaleic acid, $C_8H_4O_3 \cdot N \cdot [CH_2]_4 \cdot CO_2H$, is obtained when ethyl γ -phthaliminomalonate is hydrolysed with hydriodic acid and the resulting acid heated at 168° ; it crystallises from water in rectangular plates, m. p. 117° . The corresponding chloride,



crystallises from light petroleum in snow-white plates, m. p. $78-81^\circ$, and condenses with benzene in the presence of aluminium chloride, yielding δ -phthaliminovaleerophenone, $C_8H_4O_3 \cdot N \cdot [CH_2]_4 \cdot COPh$, which crystallises from alcohol in long, colourless prisms, m. p. $94-95^\circ$.

When hydrolysed with glacial acetic and fuming hydrochloric acids at 138° , the phthaliminoketone yields the anhydride, 2-phenyl-tetrahydropyridine, $CPh \begin{smallmatrix} \text{NH} \cdot CH_2 \\ \text{CH} \cdot CH_2 \end{smallmatrix} > CH_2$, in the form of an oil, b. p.

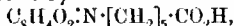
$275-277^\circ/751.5$ mm. It solidifies in a freezing mixture, and has m. p. 18° . The hydrochloride crystallises from fuming hydrochloric acid in colourless needles, m. p. $86-87^\circ$. The platinichloride forms orange-red, hexagonal plates; it sinters at 190° and melts at $191-192^\circ$, and solidifies and melts again at 202° . The aurichloride melts at 118° , after sintering at 110° . The picrate, $C_{17}H_{16}O_7N_4$, crystallises in long, yellow needles, m. p. 181° , after sintering at 160° .

When reduced with tin and hydrochloric acid, the base yields 2-phenylpyridine. This separates from its aqueous solution in colourless crystals containing $11H_2O$. The hydrate melts at $60-61^\circ$ to a turbid liquid, and, when further heated, loses water and yields the anhydrous base, $C_{11}H_{13}N$, in the form of an oil, b. p. $255-255.5^\circ/767$ mm.

The hydrochloride crystallises in hard needles, m. p. $196-197^\circ$; the platinichloride has m. p. 197° ; the aurichloride has m. p. $159-160^\circ$ and the picrate m. p. $115-116^\circ$. J. J. S.

ϵ -Amino-ketones. SIEGMUND GABRIEL and JAMES COLMAN (*Ber.*, 1908, 41, 2014—2017. Compare preceding abstract).— ϵ -Amino-ketones, unlike the corresponding γ - and δ -compounds, appear to be stable; they do not readily form anhydro-derivatives.

Ethyl phthaliminobutylmalonate (Gabriel and Maass, *Abstr.*, 1899, i, 595), when hydrolysed with hydriodic acid and the resulting dibasic acid heated at 160° , yields ϵ -phthaliminohexoic acid,

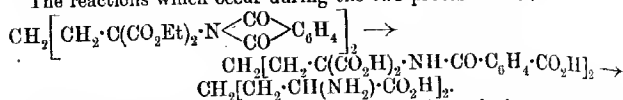


m. p. $107-107.5^\circ$. The corresponding chloride, $C_8H_4O_3 \cdot N \cdot [CH_2]_6 \cdot COCl$, melts at about 60° , and readily yields ϵ -phthaliminohexophenone, $C_8H_4O_3 \cdot N \cdot [CH_2]_6 \cdot COPh$, which crystallises from dilute alcohol in colourless plates, m. p. $90-91^\circ$. When hydrolysed at 138° with acetic and hydrochloric acids, it yields ϵ -aminohexophenone, $COPh \cdot [CH_2]_6 \cdot NH_2$, in the form of an oil. The hydrochloride has m. p. $153-154^\circ$; the platinichloride forms flat plates, and has m. p. 213° (decomp.). J. J. S.

Synthesis of Amino acids. VIII. Diaminodicarboxylic Acids and Hydroxyamino acids. SÖREN P. L. SÖRENSEN and A. C. ANDERSEN (*Zeitsch. physiol. Chem.*, 1908, 56, 250—304).—Fuller details for the preparation of $\alpha\delta$ -diaminoadipic, α -amino- γ -hydroxy-

butyric, and α -diaminopimelic acids are given (compare Abstr., 1905, i, 600). A 90% yield of diaminopimelic acid can be obtained by hydrolysing ethyl phthaliminotrimethylenedimalonate with sodium hydroxide and evaporating the product with hydrochloric acid.

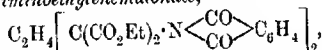
The reactions which occur during the two processes are :



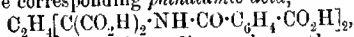
When ethyl diphthaliminoethylenemalonate is used, the first reaction proceeds in a similar manner, and a good yield of the corresponding phthalamic acid, $\text{C}_2\text{H}_4[\text{C}(\text{CO}_2\text{H})_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}]_2$, is obtained. If this is evaporated with hydrochloric acid, the yield of diaminoadipic acid is small, as secondary reactions occur. The yield can be considerably increased by first heating the hexahasic acid at $100-105^\circ$ for twenty-four hours, when carbon dioxide and a little phthalic acid are formed, and then hydrolysing with barium hydroxide and evaporating with hydrochloric acid.

In the reaction between ethyl sodiophthaliminomalonate and ethylene bromide, the yield of ethyl diphthaliminoethylenemalonate is small. Among other products formed is the lactone of ethyl phthalimino- β -hydroxyethylmalonate, obtained by the elimination of ethyl bromide from the intermediate product, ethyl phthalimino- β -bromoethylmalonate. The lactone provides a convenient material for the preparation of α -amino- γ -hydroxybutyric acid, which can be isolated in the form of its sparingly soluble benzoyl derivative. The ethyl diphthaliminoethylenemalonate is readily separated from the lactone by shaking with normal sodium hydroxide solution at the ordinary temperature and then for half-an-hour on the water-bath. Under these conditions, the lactone is dissolved, and the solution may be used for the preparation of α -amino- γ -hydroxybutyric acid.

Ethyl diphthaliminoethylenemalonate,



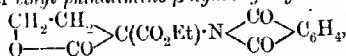
crystallises from benzene in colourless, long, thin prisms or compact crystals, m. p. $209-210^\circ$, and is insoluble in water, ether, or light petroleum. The corresponding *phthalamic acid*,



separates from solutions of its sodium salt on the addition of well-cooled hydrochloric acid in the form of compact, rectangular crystals containing $2\text{H}_2\text{O}$. When quickly heated, it has m. p. 240° (decomp.), but also decomposes at 210° .

$\alpha\delta$ -Diaminoadipic acid is practically insoluble in the ordinary neutral solvents, but dissolves in 5*N*-sulphuric or hydrochloric acid; it does not melt at 275° , but, when heated for some time at this temperature, slowly decomposes. Its *benzoyl* derivative has m. p. $270-275^\circ$, and is sparingly soluble in all ordinary solvents.

The lactone of *ethyl phthalimino- β -hydroxyethylmalonate*,



crystallises from alcohol in flat prisms, m. p. 132° . When the

alkaline solution is evaporated with hydrochloric acid, it yields α -amino- γ -hydroxybutyrolactone, the benzoyl derivative of which has m. p. 145° (compare Fischer and Blumenthal, Abstr., 1907, i, 191). The dibenzoyl derivative of α -amino- γ -hydroxybutyric acid can be obtained from the oily products formed in the preparation of ethyl diphthaliminoethylenemalonate, and has m. p. 210—211°.

Ethyl diphthaliminotrimethylenemalonate crystallises from absolute alcohol in flat, lens-shaped needles, m. p. 149°. *ac*-Diaminopimelic acid, $C_8H_{14}O_4N_2$, crystallises from aqueous alcohol in slender needles, it does not melt at 300°, and has no sweet taste. It is readily precipitated by phosphotungstic acid. Its dibenzoyl derivative, $C_{21}H_{22}O_6N_2$, crystallises from 25% alcohol in minute needles, m. p. 220°.

The benzoylation of certain aminohydroxy- and diamino-acids has been studied under varying conditions. When an excess of sodium hydroxide is used, so that the liquid during the process is always about 0.5*N* as regards the alkali, it is found that aminohydroxy-acids yield monobenzoyl derivatives only. When, on the other hand, the solution is kept practically neutral, a mixture of mono- and di-benzoyl derivatives is obtained. The benzoyl derivatives of hippuric acid and of diamino-acids are not affected by warming with *N*/20-sodium hydroxide solution; under the same conditions, the dibenzoyl derivatives of aminohydroxy-acids are hydrolysed to monobenzoyl derivatives.

Monobenzoyl α -amino- δ -hydroxyvaleric acid has been obtained in a crystalline form with m. p. about 170°.

Monobenzoyl α -amino- γ -hydroxyvaleric acid has m. p. about 138° (Fischer and Blumenthal, *loc. cit.*, 121°). Its barium salt is sparingly soluble.

J. J. S.

4-Amino-*o*-phthalic Acid and Some of its Derivatives.

MARSTON T. BOGERT and ROSEMER REX RENSUAW (*J. Amer. Chem. Soc.*, 1908, 30, 1135—1144).—In an earlier paper (Abstr., 1906, i, 510), methyl 4-aminophthalate and some of its derivatives were described. A description is now given of the acid, its salts, and certain derivatives.

It has been found by Miller (Abstr., 1882, 404) that on reducing 4-nitrophthalic acid with tin and hydrochloric acid and treating the product with hydrogen sulphide, *m*-aminobenzoic acid is produced; this result is now confirmed. The method described by Seidel (Abstr., 1902, i, 160) for preparing 4-aminophthalic acid by reducing the nitro-compound with sodium sulphide does not readily afford a good yield. The acid can be easily prepared, however, by the hydrolysis of the dimethyl ester or of 4-nitrophthalimide.

4-Aminophthalic acid forms colourless, microscopic plates; when heated, it loses water and changes into a yellowish-grey, infusible residue. If the acid is boiled with hydrochloric acid, it is converted into *m*-aminobenzoic acid. On diazotising 4-aminophthalic acid and adding the product to a warm copper potassium cyanide solution, a yellow, granular compound, m. p. 166° (corr.), is produced, which is probably the 4-monoamide of trimellitic acid, and small quantities of another substance, possibly trimellitic acid, are formed simultaneously.

The *hydrochloride* of 4-aminophthalic acid, the *sodium*, *potassium*, *ammonium*, *calcium*, *barium*, *nickel*, *copper*, *lead*, and *silver* salts, and the *mercuric chloride* double salt are described. The *anhydride*,

$\text{NH}_2 \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{CO} \\ \diagup \diagdown \\ \text{CO} \end{smallmatrix} \text{O}$, obtained by heating the acid at 180—200° for two hours, is a pale salmon-coloured, infusible solid. 4-Acetylaminophthalic

anhydride, $\text{NHAc} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{CO} \\ \diagup \diagdown \\ \text{CO} \end{smallmatrix} \text{O}$, m. p. 206—207° (corr.), obtained by

the action of acetic anhydride or acetyl chloride on the amino-acid, forms microscopic needles. 4-Aminophthalimide, m. p. 234° (corr.), prepared by reducing 4-nitrophthalimide with stannous chloride, crystallises in golden-yellow needles; its *hydrochloride* forms grey

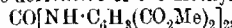
crystals. The *methylimide*, $\text{NH}_2 \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{CO} \\ \diagup \diagdown \\ \text{CO} \end{smallmatrix} \text{NMe}$, m. p. 242—243°

(corr.), forms yellow crystals; its *hydrochloride* crystallises in plates.

4-Nitrophthalimethylimide, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{CO} \\ \diagup \diagdown \\ \text{CO} \end{smallmatrix} \text{NMe}$, m. p. 179—180°

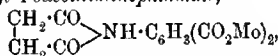
(corr.), forms long, white needles. 4-Aminophthalanil has m. p. 205.5°

(corr.). The *carbamide* derivative of the methyl ester,



m. p. 213—214° (corr.), prepared by the action of carbonyl chloride on a pyridine solution of the methyl ester, crystallises in short needles.

Methyl 4-ethyloxalylaminophthalate (Abstr., 1906, i, 510) has m. p. 126° (corr.). Methyl 4-succiniminophthalate,



m. p. 153.4° (corr.), forms large, colourless prisms or needles. Methyl

4-phthaliminophthalate, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \diagdown \\ \text{CO} \end{smallmatrix} \text{N} \cdot \text{C}_6\text{H}_3(\text{CO}_2\text{Me})_2$, m. p. 174° (corr.),

crystallises in long, colourless needles.

E. G.

Constitution of Phthalein Salts. RICHARD MEYER and KARL MARX (*Ber.*, 1908, 41, 2446—2453).—The results published previously (Abstr., 1907, i, 932) have been confirmed. The absorption spectra of aqueous solutions of the sodium salts of phenolphthalein, tetrabromophenolphthalein, quinolphthalein, fluorescein, and eosin have been compared. The curves obtained on plotting the concentrations against the wave-lengths are similar for all five compounds. The conclusion is drawn therefore that the salts of these substances must have a similar quinonoid structure, the difference in colour being merely one of degree.

The *potassium* salt of phenolphthalein, $\text{C}_{20}\text{H}_{12}\text{O}_4\text{K}$, forms a deliquescent, deep red mass; the *sodium* salt, $\text{C}_{20}\text{H}_{12}\text{O}_4\text{Na}$, is almost black with a metallic glance.

W. H. G.

Theory of Indicators. SALOMON F. ACREE (*Amer. Chem. J.*, 1908, 39, 649—650). JULIUS STIEGLITZ (*ibid.*, 651—653).—With reference to this controversy (compare Abstr., 1904, ii, 17; this vol., i, 423), the authors, starting from different points of view, have now come to similar conclusions regarding the theory of indicators. These conclusions have been already put forward (this vol., i, 423).

E. G.

Theory of Indicators and the Reactions of Phthaleins and their Salts. II. SALOMON F. ACREE and E. A. SLAGLE (*Amer. Chem. J.*, 1908, 39, 789—791).—Acree (this vol., i, 423) has stated that the chief source of the colour of salts of the phthaleins is the phenol salt of a quinone compound.

It is now pointed out that Orndorff has obtained coloured salts of trimethylgallein and its tetrachloro-derivative, whilst such substances as phenolphthalein methyl ether and tetrabromophenolphthalein ethyl ether dissolve in alkalis to form colourless solutions. The sodium salt of fluorescein ethyl ether yields an aqueous solution which is much less intensely coloured than are solutions of fluorescein salts. The alcoholic solution of this salt is only faintly coloured at from -15° to 0° , but the colour increases as the temperature is raised to 80° , and decreases again as the temperature is lowered. When this sodium salt is treated with ethyl iodide, it yields a mixture of the colourless phenolic diethyl ether and the coloured quinonoid diethyl ether.

All these facts are discussed in the light of Acree's theory (*loc. cit.*), and are shown to be readily capable of explanation. E. G.

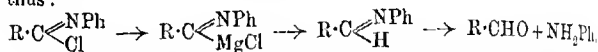
Conversion of Carboxylic Acids into their Aldehydes. GEORG MERLING (*Ber.*, 1908, 41, 2064—2066).—In the course of his studies on the synthesis of perfumes, the author has repeatedly found it necessary to convert hydroaromatic acids into the corresponding aldehydes. As the reactions employed previously for such conversion give only poor yields and are therefore unsuitable for the purpose, a new method was required. One giving in the case of hydroaromatic acids 50% to 80% yields of the aldehyde has now been found in the following series of changes. The carboxylic acid, $R\cdot CO_2H$, is converted by way of the chloride, $R\cdot COCl$, anilide, $R\cdot CO\cdot NHPh$, and phenylimide chloride, $R\cdot CCl\cdot NPh$, into the diphenylamidine, $R\cdot C(NPh)\cdot NHPh$, which is reduced by means of sodium and alcohol to the diphenylmethylenediamine, $R\cdot CH(NHPh)_2$; this, when heated with dilute mineral acids, is hydrolysed, forming the aldehyde, $R\cdot CHO$, and aniline. The method is less suitable for the formation of aldehydes from aromatic or aliphatic acids; benzaldehyde is obtained from benzoic acid in only a 20% yield, whilst with many aliphatic acids the yield of aldehyde is still smaller. The amount of aldehyde formed appears to depend on the stability of the diphenylmethylenediamine; in many cases, this is decomposed by the reducing agent with formation of the Schiff's base, $R\cdot CH\cdot NPh$, which is then further reduced, and hence does not yield the aldehyde on hydrolysis.

Δ^3 -cycloGeranic acid, $CH\begin{smallmatrix} \diagup CH_2-CMe_2 \\ \diagdown CH_2-CHMe \end{smallmatrix} > CH\cdot CO_2H$, prepared by fission of water from ketodihydrocyclogeranic acid (*Abstr.*, 1905, i, 349), is obtained in two stereoisomeric forms, m. p. $75-76^{\circ}$ and m. p. $83-84^{\circ}$, which form two anilides, m. p. 178° and m. p. $143-145^{\circ}$ respectively. Δ^3 -cycloCitral, $C_{10}H_{16}O$, obtained in a 60—70% yield from the anilide, m. p. 178° , is an oil, b. p. $53-54^{\circ}/4$ mm. or $76^{\circ}/12$ mm., and has a suffocating odour of carvone.

α -cycloGeranic acid yields an anilide, m. p. $157-158^{\circ}$, from which a mixture of α - and β -cyclocitral is obtained in a 60—80% yield. Whilst

the conversion of α -cyclogeranic acid into the aldehyde is thus accompanied by a transmigration of the ethylene linking, β -cyclogeranic acid, is converted by way of the *anilide*, m. p. 162°, into β -cyclocitral only.
G. Y.

Transformation of Carboxylic Acids into their Aldehydes. HERMANN STAUDINGER (*Ber.*, 1908, 41, 2217—2219. Compare Merling, preceding abstract).—Carboxylic acids may be converted into their corresponding aldehydes as follows: the imide chloride is treated with magnesium, whereby a Grignard compound is formed; water decomposes the latter, yielding a Schiff's base, from which the aldehyde is obtained by treatment with dilute hydrochloric acid, thus:



The reaction has been carried through with the imide chloride obtained from benzanilide. The imide chlorides derived from oxanilide and isobutyranilide react with magnesium, but the aldehydes have not been obtained.

The *imide chloride*, $\text{CHMe}_2\cdot\text{CCl}\cdot\text{NPh}$, prepared by acting on isobutyranilide with phosphorus pentachloride, is a colourless liquid, b. p. 101—103°/13 mm., which decomposes slowly.

The *imide chloride*, $\text{CHPh}_2\cdot\text{CCl}\cdot\text{NPh}$, derived from diphenylacetanilide, forms compact crystals, m. p. 94—95°. W. H. G.

Anisylidene Chloride. HANS SCHMIDT (*Ber.*, 1908, 41, 2331—2332. Compare Hoering and Baum, this vol., i, 527).—*Anisylidene chloride* is probably formed by the action of phosphorus pentachloride on anisaldehyde, but is best prepared by boiling 1 mol. of anisaldehyde with a little more than 1 mol. of thionyl chloride and about an equal volume of benzene for several hours under reflux, with exclusion of moisture. It has m. p. 20°, b. p. 130—132°/13 mm. 134°/14 mm., and is unstable. It is readily hydrolysed by cold water or alcoholic potash with formation of anisaldehyde. J. C. C.

Preparation of Aromatic Hydroxyaldehydes and Partially Alkylated Polyhydroxyaldehydes by Fission of the Corresponding Alkyl Derivatives. CAMILLE DREYFUS (*D.R.P.* 193958).—The well-known action of aluminium chloride on mixed ethers, such as phenetole, has been examined in the case of aromatic aldehydes containing alkoxyl groups, with the result that these substances have been converted into the corresponding hydroxyaldehydes.

Veratraldehyde, when dissolved in benzene or toluene and treated with re-sublimed aluminium chloride, furnishes a mixture of 3-dihydroxybenzaldehyde, 4-hydroxy-3-methoxybenzaldehyde, and isovanillin.

Anisaldehyde, when similarly treated, yields *p*-hydroxybenzaldehyde. G. T. M.

New Cyclic Ketones. GUSTAVE BLANC (*Bull. Soc. chim.*, 1908, [iv], 3, 780—786).—These ketones were prepared by the process

already given (Abstr., 1907, i, 710), namely, by heating the corresponding substituted adipic or pimelic acid with acetic anhydride and distilling the anhydride first formed. 1:1-Dimethylcyclopentan-5-one, b. p. 143°, prepared from $\alpha\alpha$ -dimethyladipic acid (Abstr., 1906, i, 523), furnishes an *oxime*, m. p. 69°, which crystallises from light petroleum. When condensed with benzaldehyde in presence of alcohol and sodium hydroxide, the ketone gives 1:1-dimethyl-4-benzylidenecyclopentan-5-one, m. p. 36°, which separates from light petroleum in bulky crystals. 1-*iso*Propylcyclopentan-5-one, obtained from *isopropyladipic acid* (Abstr., 1905, i, 681), yields a semicarbazone, m. p. 199—200° (compare Bouveault and Locquin, this vol., i, 173). 1:1-Dimethylcyclopentan-4-one, b. p. 153—154°, obtained from $\beta\beta$ -dimethyladipic acid, is a mobile liquid, and has an odour of camphor, benzaldehyde, and menthone; its *semicarbazone*, m. p. 178—179°, crystallises from methyl alcohol in colourless needles. 1:1-Dimethylcyclohexan-5-one, obtained from $\beta\beta$ -dimethylpimelic acid (compare Leser, Abstr., 1899, i, 743), gives a semicarbazone, m. p. 203°, which crystallises in colourless needles. The 2-(or 4)-benzylidene derivative of the ketone, m. p. 56°, separates from light petroleum in bulky, nearly colourless crystals. On reduction with sodium and alcohol, the ketone yields the corresponding hexanol (Crossley and Renouf, Trans., 1905, 87, 1487). 1:1:4-Trimethylcyclohexane-5-one semicarbazone (Abstr., 1907, i, 710) crystallises in colourless needles. T. A. H.

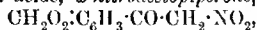
Products of Condensation of *o*- and *p*-Nitrobenzyl Chlorides with Acetylacetone. H. MECH (*Compt. rend.*, 1908, 146, 1409—1411).—The author has prepared derivatives of δ -*p*-nitrophenyl- β -butanone and of di-*o*-nitrobenzylacetylacetone which he described recently (Abstr., 1907, i, 63).

δ -*p*-Nitrophenyl- β -butanone semicarbazone is a white powder, m. p. 198.5°. When δ -*p*-nitrophenyl- β -butanone is reduced with zinc and hydrochloric acid, it yields δ -*p*-aminophenyl- β -butanone as a yellow mass, m. p. about 195° (decomp.). The *semicarbazone* forms colourless crystals, m. p. 153° (decomp.).

From the oil obtained along with di-*o*-nitrobenzylacetylacetone, it was not possible to isolate δ -*o*-nitrophenyl- β -butanone, but the *oxime*, m. p. 97°, and the *semicarbazone*, m. p. 169—170°, were prepared.

J. C. C.

Preparation of ω -Nitroacetocatechol. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 195814).—When piperonaldehyde is treated successively with nitromethane, bromine, methyl-alcoholic potash, and acids, ω -nitroacetopiperone,



is obtained, yellow leaflets or needles, m. p. 173°. ω -Nitroacetoveratrone, $\text{C}_6\text{H}_3(\text{OMe})_2\text{CO}\cdot\text{CH}_2\cdot\text{NO}_2$, needles, m. p. 144°, is produced from veratraldehyde by a similar series of operations. These nitrated ketones, on treatment with aluminium chloride in benzene or toluene, lose their methylene and methyl groups respectively, and give rise to ω -nitroacetocatechol, $\text{C}_6\text{H}_3(\text{OH})_2\text{CO}\cdot\text{CH}_2\cdot\text{NO}_2$, yellow crystals, blackening at 170—180°, and decomposing at 188°. On

reduction, this compound furnishes aminoacetocatechol, which is of importance in connexion with the synthesis of bases of the adrenaline group.

G. T. M.

Identity of Methysticol and Piperonyleneacetone. ERICH WINZHEIMER (*Ber.*, 1908, 41, 2377—2883).—According to Pomeranz (*Abstr.*, 1889, 278; 1890, 257), methysticol, a derivative of mothysticin obtained from *Piper methysticum*, is identical with piperonyleneacetone, $\text{CH}_3\text{:O}_2\text{:C}_6\text{H}_4\text{:CH:CH:CH:CH:COMe}$, synthesised by Scholtz (*Abstr.*, 1895, i, 469). Pomeranz, however, states that methysticol has m. p. 94° and is readily soluble in alcohol and ether, whilst Scholtz's compound is described as having m. p. 89° and being only slightly soluble in these solvents. The present author, having obtained a quantity of methysticol in the course of other work, has prepared piperonyleneacetone, and on comparison finds the two substances to be identical, having m. p. $89.5\text{--}90^\circ$ separately and when mixed. The phenylhydrazone has m. p. $152\text{--}152.5^\circ$ (141° : Scholtz, *loc. cit.*); the semicarbazone, m. p. $199\text{--}199.5^\circ$; the benzylidene derivative, $\text{C}_{20}\text{H}_{16}\text{O}_3$, golden needles, m. p. $110\text{--}111^\circ$; forms a phenylhydrazone, crystallising in golden needles, m. p. $187.5\text{--}188^\circ$. The piperonylidene derivative, $\text{C}_{21}\text{H}_{16}\text{O}_2$, yellow needles, m. p. 195° .

Dipiperonyleneacetone (piperonylenemethysticol) has m. p. $203\text{--}204^\circ$ ($198\text{--}199^\circ$: Scholtz).

The following derivatives of piperonylacetaldehyde were prepared; the m. p. in brackets; are those given by Ladenburg and Scholtz (*Abstr.*, 1895, i, 42) or by Scholtz and Kipke (*Abstr.*, 1904, i, 508). The phenylhydrazone, m. p. $163\text{--}164^\circ$ (160°); the semicarbazone, m. p. 234° (226°); *o*-toluidide, m. p. $92\text{--}92.5^\circ$ ($94\text{--}95^\circ$); *p*-toluidide, m. p. $139.5\text{--}140.5^\circ$ (138°); acetophenone derivative, m. p. 137.5° (133°).

G. Y.

Derivatives of Phenyl β -Naphthyl Ketone. GUSTAVE PERRIER and CAILLE (*Bull. Soc. chim.*, 1908, [iv], 3, 736—739).—Phenyl β -naphthyl ketone, regenerated from its additive product with aluminium chloride (*Abstr.*, 1896, i, 353), furnishes (1) an oxime, m. p. 133° , which separates from alcohol in colourless, silky crystals and is insoluble in water, soluble in alcohol or toluene, and scarcely so in light petroleum; (2) a phenylhydrazone, m. p. 123° , which forms faintly yellow crystals from alcohol, reddens slightly on exposure to air, is paramagnetic, and gives a green coloration with sulphuric acid, and (3) a semicarbazone, m. p. 175° , which forms colourless crystals from alcohol. On reduction with sodium amalgam in alcohol at 60° , the ketone furnishes phenylnaphthylcarbinol, m. p. 83° , which crystallises from alcohol in colourless, silky needles and is diamagnetic; the benzoyl derivative, m. p. 110° , forms silky needles from alcohol and is diamagnetic. With the exception of the phenylhydrazone, all these derivatives, like the ketone, give red or orange-red colorations with sulphuric acid.

T. A. H.

Preparation of 3:4-Dihydroxyphenylglyoxime and 3:4-Dihydroxyphenylalkylglyoximes. CHEMISCHE FABRIK AUF ACTIEN (vorm. E. SCHERING) (D.R.-P. 195655, 195656, 195657).—When treated with excess of hydroxylamine, preferably on warming, the 3:4-dihydroxyphenyl alkyl ketones of the type $C_6H_3(OH)_2 \cdot CO \cdot CHXR$ (where X is hydrogen or alkyl and R a halogen) give rise to substituted glyoximes having the general formula $C_6H_3(OH)_2 \cdot C(NO\dot{H}) \cdot CX \cdot NO\dot{H}$. These products are of importance as the starting point in the preparation of bases having haemostatic properties.

3:4-Dihydroxyphenylglyoxime, $C_6H_3(OH)_2 \cdot C(NO\dot{H}) \cdot CH \cdot NO\dot{H}$, white needles, m. p. 185–186°, is produced by warming ω -chloroacetocatechol with an aqueous solution containing hydroxylamine hydrochloride and sodium carbonate. This compound is also produced by the action of hydroxylamine on ω -aminoacetocatechol or dimethyl- or diethyl- ω -aminoacetocatechol. This reaction is especially remarkable, as it does not take place with aminoacetone or the dialkylaminoacetones.

This condensation occurs most readily in dilute acetic acid, and may also be effected with methyl- ω -aminoacetocatechol and piperidylacetocatechol.

4:4-Dihydroxyphenylmethylglyoxime,
 $C_6H_3(OH)_3 \cdot C(NO\dot{H}) \cdot CMe \cdot NO\dot{H}$,
 white needles, m. p. 201–202°.

G. T. M.

Constitution of Some Derivatives of Diphenylmethane and Preparation of Some *o*-Diamino-compounds of the Same Series. HENRI DUVAL (*Compt. rend.*, 1908, 146, 1324–1326).—The constitution of acetyldiphenylmethane and dinitrodiphenylmethanedicarboxylic acid, described previously (this vol., i, 277), and of dinitroacetyldiphenylmethane is established.

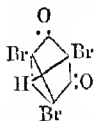
The first compound must be 4-acetyldiphenylmethane, since, on oxidation, it gives benzophenone-4-carboxylic acid. When 2:2'-dinitro-4:4'-diaminodiphenylmethane is converted through the diazo-reaction into the corresponding dinitrile and the latter hydrolysed, the 2:2'-dinitrodiphenylmethane-4:4'-dicarboxylic acid produced is identical with the acid formed by nitrating diphenylmethane-4:4'-dicarboxylic acid.

When 4:4'-diacetyldiphenylmethane is nitrated at -10° with colourless nitric acid in the presence of sulphuric acid, 2:2'-dinitro-4:4'-diacetyldiphenylmethane, $CH_2(C_6H_3Ac \cdot NO_2)_2$, is formed in yellowish-white needles, m. p. 151°, which give an *oxime*, m. p. 224°. The position of the nitro-groups in this compound is fixed by the facts that on oxidation by sodium hypobromite and esterification of the resulting acid, the ester produced is identical with that formed by the oxidation of ethyl 2:2'-dinitrodiphenylmethane-4:4'-dicarboxylate, and that 2:2'-dinitrodiphenylmethane-4:4'-dicarboxylic acid is produced by the prolonged action of a mixture of nitric and sulphuric acids on 4:4'-diacetyldiphenylmethane. 2:2'-Diamino-4:4'-diacetyldiphenylmethane is formed by reducing the corresponding dinitro-derivative, and crystallises in yellow needles, m. p. 166°. When 2:2'-dinitro-4:4'-diaminodiphenylmethane is diazotised and treated with

cuprous cyanide, 2:2'-dinitro-4:4'-dicyanodiphenylmethane,

$\text{CH}_2[\text{C}_6\text{H}_3(\text{NO}_2)_2\text{CN}]_2$, bright yellow crystals, m. p. 195° , is formed. This on reduction gives 2:2'-diamino-4:4'-dicyanodiphenylmethane, yellow crystals, m. p. 236° . 2:2'-Dinitro-4:4'-diacetyldiaminodiphenylmethane, yellow crystals, m. p. 229° , is formed by the action of acetic anhydride on the amine, and when reduced gives 4:4'-diacetyl-2:4:2':4'-tetra-aminodiphenylmethane, $\text{CH}_2[\text{C}_6\text{H}_3(\text{NHAc})\text{NH}_2]_2$, white needles, m. p. 244° . E. H.

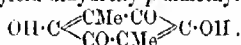
Tribromoresoquinone [*m*-Benzoquinone]. RICHARD MEYER and KURT DESAMARI (*Ber.*, 1908, 41, 2437—2445).—Experiments are being made with the object of preparing simple meta quinones. The present communication deals with the meta-quinone first described by Leibermann and Dittler (*Journ.*, 1872, 297), namely, tribromoresoquinone. This compound has been carefully analysed and its mol.-wt. determined; the results obtained show definitely that the compound has the molecular formula $\text{C}_6\text{H}_2\text{O}_2\text{Br}_3$, and not the bimolecular formula proposed by Benedikt (*Abstr.*, 1879, 55, 464, 717), and that its chemical properties are best represented by the annexed formula. Tribromoresoquinone possesses the characteristic properties of quinones; thus it liberates iodine from potassium iodide.



It is reduced when treated with hydroxylamine and phenylhydrazine, yielding tetrabromodiresorcinol (compare Benedikt, *loc. cit.*). The results of mol.-wt. determinations agree with the formula $\text{C}_{12}\text{H}_6\text{O}_4\text{Br}_4$ assigned by Benedikt to this compound.

W. H. G.

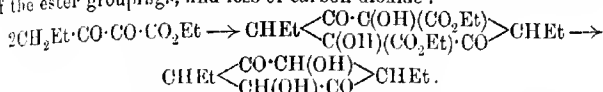
Synthetical *p*-Dialkylated Dihydroxyquinones. FRITZ FICHTER (*Annalen*, 1908, 361, 363—402).—It was shown previously (Fichter and Willmann, *Abstr.*, 1904, i, 678) that certain red, crystalline by-products, obtained when metallic sodium is used instead of sodium ethoxide as the condensing agent in the synthesis of ethyl alkyloxalacetates from ethyl oxalate and esters of monobasic fatty acids, are dihydroxyquinones derived from *p*-dialkylbenzenes. Thus ethyl oxalate and ethyl propionate yield dihydroxy-*p*-dimethylbenzoquinone,



The mechanism of the synthesis has now been studied, and a number of derivatives and hydrolysis products of dihydroxy-*p*-dialkylbenzoquinones are described.

The dihydroxy-*p*-dialkylbenzoquinones cannot be formed by way of the ethyl alkyloxalacetates, since they are obtained only when sodium is employed as condensing agent, whereas the ethyl alkyloxalacetate formation takes place most easily with sodium ethoxide; on the other hand, ethyl oxalate and ethyl acetate do not form a dihydroxybenzoquinone even with sodium. Moreover, whilst the formation of ethyl alkyloxalacetates takes place only with ethyl propionate and ethyl butyrate, and not with ethyl isovalerate, dihydroxybenzoquinones are formed, not only from these three esters, but also from ethyl *n*-hexoate, *n*-heptoate, phenylacetate, and hydrocinnamate. According to Claisen's view of the action of sodium on ethyl isobutyrate (*Abstr.*, 1897, i, 592),

the first product of the condensation of ethyl oxalate and ethyl butyrate by means of sodium must be an $\alpha\beta$ -diketonic ester, formed according to the scheme: $\text{CH}_3\text{Et}\cdot\text{CO}_2\text{Et} + \text{C}_2\text{O}_4\text{Et}_2 + \text{Na}_2 = \text{CH}_3\text{Et}\cdot\text{CO}\cdot\text{CO}\cdot\text{CO}_2\text{Et} + 2\text{NaOEt}$. In agreement with this, it is found that the yield of dihydroxyquinone is greater when 1 mol. than when 1 atom of sodium is employed for the condensation of 1 mol. of ethyl oxalate with 1 mol. of ethyl butyrate, whereas 1 atom of sodium suffices for the oxalacetate synthesis with the same amount of two esters. It is considered that the synthesis under discussion takes place by way of the $\alpha\beta$ diketonic ester, which undergoes ring condensation, hydrolysis of the ester groupings, and loss of carbon dioxide:



1. *Synthesis of Dihydroxy-p-dialkylbenzoquinones.*—[With EUGEN WEISS.]—The following derivatives of dihydroxy-*p*-dialkylbenzoquinones, previously described, have now been prepared.

Dihydroxy-p-xylquinone diacetate, $\text{C}_{12}\text{H}_{12}\text{O}_6$, crystallises in yellow needles, m. p. 146.5° , and on reduction with zinc dust and glacial acetic acid yields *tetra-acetoxy-p-xylene*, $\text{C}_{12}\text{H}_4\text{O}_8$, crystallising in white needles, m. p. 242° .

Dihydroxy-p-diisopropylbenzoquinone dibenzoate, $\text{C}_{26}\text{H}_{24}\text{O}_6$, crystallises in yellow needles, m. p. 220° .

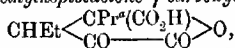
Dihydroxy-p-di-n-butylbenzoquinone, $\text{C}_{24}\text{H}_{20}\text{O}_4$, prepared from ethyl oxalate and ethyl *n*-hexoate, separates from glacial acetic acid in red crystals, m. p. 175° in a sealed capillary tube, forms in aqueous alkalis a violet, in concentrated sulphuric acid a dark blue solution, and when boiled with aqueous sodium hydroxide undergoes the succinic acid hydrolysis. The *diacetate*, $\text{C}_{28}\text{H}_{24}\text{O}_6$, forms yellow needles, m. p. 60° .

Dihydroxy-p-diphenylbenzoquinone, $\text{C}_{18}\text{H}_{12}\text{O}_4$, prepared from ethyl phenylacetate and ethyl oxalate, forms violet-brown crystals, decomp. $280\text{--}300^\circ$, gives with aqueous alkalis a violet, with concentrated sulphuric acid a brown coloration, and dyes mordants more feebly than the dialkyl compounds.

Dihydroxy-p-dibenzylbenzoquinone, $\text{C}_{20}\text{H}_{16}\text{O}_4$, prepared from ethyl hydrocinnamate and ethyl oxalate, crystallises in red leaflets, m. p. 225° in a sealed tube, gives colorations similar to those of the preceding substance, and is a strong dye. The *diacetate*, $\text{C}_{24}\text{H}_{20}\text{O}_6$, forms yellow needles, m. p. 182° .

2. *Synthesis of Dihydroxy-p-dialkylquinones.*—[With MAX JETZER.]—Comparative experiments on the influence of different solvents and of different alkyl groups on the formation of dihydroxy-*p*-dialkylbenzoquinones show that better yields are obtained in benzene or toluene than in ethereal solution, that methyl oxalate and methyl butyrate give better yields than the ethyl or *isoamyl* esters, and that ethyl oxalate condensed with methyl *isovalerate* gives a better yield of the dihydroxybenzoquinone than a mixture of the methyl esters, a mixture of the ethyl esters, or a mixture of methyl oxalate with ethyl *isovalerate*. The reaction takes place more easily with the *isovalerate* than with the butyrate.

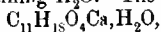
8. *Hydrolysis of Dihydroxy-p-dimethylquinone and Dihydroxy-p-diethylbenzoquinones.*—[With HANS KAPPELER.]—When boiled with sodium hydroxide in aqueous solution, dihydroxy-p-xyloquinone yields *s*-methyl-ethylsuccinic acid, m. p. 178°, and *as*-methylethylsuccinic acid, m. p. 99—100°. These two acids are obtained also by the hydrolysis of α -keto- β -methylhexolactone- γ -carboxylic acid (Fichter and Preiswerk, Abstr., 1902, i, 443) by means of boiling 5% sodium hydroxide. The hydrolysis of dihydroxy-p-diethylbenzoquinone in the same manner leads to the formation of *s*-ethylpropylsuccinic acid, $C_9H_{16}O_4$, m. p. 174—175°, which forms a barium salt, $C_9H_{14}O_4Ba, H_2O$, and an ethyl ester, $C_{13}H_{24}O_4$, colourless oil, b. p. 131—135°/16 mm., and as *ethylpropylsuccinic acid*, which crystallises in stellate aggregates, m. p. 97—98°. These ethylpropylsuccinic acids are obtained also by hydrolysis of α -keto- β -ethylheptolactone- γ -carboxylic acid,



which is formed by heating butyrylformic acid with 75% sulphuric acid, crystallises in colourless needles, m. p. 110—111°, and gives an intense red coloration with ferric chloride.

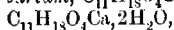
4. *Hydrolysis of Dihydroxy-p-diisopropylbenzoquinone and Dihydroxy-thymoquinone.*—[With HEINRICH GLASER.]—The hydrolysis of dihydroxy-p-diisopropylbenzoquinone with boiling dilute sodium hydroxide leads to the formation of two isopropylisobutylsuccinic acids, which are not identical with Beatty's acids (Abstr., 1903, i, 726).

*iso*Propylisobutylsuccinic acid, $C_{11}H_{20}O_4$, m. p. 185—186°, crystallises from hot water in colourless needles, or from cold water separates in crystals containing H_2O . The calcium salt,



is colourless. The *anhydride*, $C_{11}H_{18}O_3$, formed by boiling the acid with acetic anhydride, is obtained as a colourless oil, b. p. 150°/12 mm., and when boiled with water yields the acid, m. p. 185—186°.

*iso*Propylisobutylsuccinic acid, m. p. 124°, crystallises from water in cubes, is volatile with steam, and can be extracted from the aqueous distillate by ether. The barium, $C_{11}H_{18}O_4Ba, 2H_2O$, and calcium,



salts were analysed. The *anhydride* is formed when the anhydride of the acid of higher m. p. is distilled under the ordinary pressure; it is a slightly yellow liquid, b. p. 264—265°, and when boiled with water yields the acid, m. p. 124°. When heated with 18% hydrochloric acid at 180—220°, the acid, m. p. 124, is converted into the acid, m. p. 185—186°.

Diethyldiaminothymoquinone, $C_{14}H_{22}O_2N_2$, prepared from ethylamine, forms violet-red needles, m. p. 116°.

On hydrolysis with sodium hydroxide, dihydroxythymoquinone yields two *ethylisopropylsuccinic acids*, $C_9H_{16}O_4$. *Ethylisopropylsuccinic acid*, m. p. 210°, crystallises from water in colourless needles, and forms a calcium salt, $C_9H_{14}O_4Ca, H_2O$. This acid can be prepared also by condensation of ethyl ethylmalonate with ethyl α -bromoisovalerate by means of sodium; the intermediate *ethyl tricarboxylate*,



has b. p. 164°/12 mm.

Ethylisopropylsuccinic acid, m. p. 96°, crystallises in cubes; the calcium salt, $C_8H_{14}O_5Ca.H_2O$, forms long needles.

Dihydroxytoluquinones are best prepared by the action of methylamine on toluquinone and hydrolysis of the tetra-acetate of this, when the resulting tetrahydroxytoluene is rapidly oxidised by air to the dihydroxytoluquinone.

Di-p-methylaminotoluquinone, $NHMe \cdot C_6H_3(NO_2)Me \cdot NHMe$, forms a brown, crystalline powder, m. p. 235°. The *tetra-acetate*, $C_6HMe(OAc)_4$,

crystallises in needles, m. p. 198°. This tetra-acetate differs from the dialkylated compounds in that its alkaline solution does not become colourless even on prolonged boiling; the product is a black, syrupy mass, from which a crystalline acid could not be isolated. G. Y.

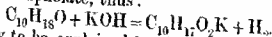
Preparation of $\alpha\beta$ -Dihydroxyanthraquinones and $\alpha\beta$ -hydroxyanthraquinonesulphonic Acids. R. WEDEKIND & Co. D.R.P. 195874).—The 1:6- and 1:7-anthraquinonesulphonic acids when heated under pressure with water, calcium hydroxide, potassium nitrate, and calcium chloride yield a mixture of 1:6- and 1:7-dihydroxyanthraquinones and an intermediate hydroxyanthraquinonesulphonic acid.

G. T. M.

Preparation of Halogen Derivatives of Benzanthrone, ADISCHE ANILIN- & SODA FABRIK (D.R.-P. 193959. Compare Abstr., 1907, i, 324).—A *bromobenzanthrone*, yellow needles or leaflets, m. p. 76°, is obtained by brominating benzanthrone in acetic acid solution. Chlorination of benzanthrone in the same medium leads to the formation of two dichlorobenzanthrones, which are separated by fractional crystallisation from acetic anhydride, glacial acetic acid, or nitrobenzene; these isomerides crystallise in yellow needles, and melt respectively at 269° and 218°. By chlorinating benzanthrone with titanium chloride and hydrochloric acid in 50% acetic acid, a *monobenzanthrone* is obtained, golden-yellow needles m. p. 176°. *monobenzanthronequinoline*, golden-yellow needles, m. p. 298°, is induced by brominating benzanthronequinoline. These products differ from those obtained by condensing the halogenated anthraquinones with glycerol in containing the halogen in the anthrone ring. On oxidation, they furnish anthraquinone-1-carboxylic acid, whereas the former series give rise to the halogen derivatives of this acid.

G. T. M.

Direct Transformation of Borneol into Campholic and *iso*Campholic Acids. MARCEL GUERRET (*Compt. rend.*, 1908, 147, 70–72. Compare Abstr., 1901, i, 307).—When borneol is heated at 250–280° in sealed tubes with recently-fused potassium hydroxide, it is almost completely transformed into a mixture of potassium campholate and *iso* campholate, thus:



This is probably to be explained by the rupture of one of the rings in borneol in two different ways, one giving campholic, and the other *iso*-campholic, acid. The two acids are readily separated, since the former

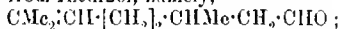
is precipitated from its alkaline solutions by carbon dioxide, and, moreover, it is not esterified by hydrochloric acid and alcohol.

The campholic acid obtained has $\alpha + 46.6^\circ$, differing somewhat from the value $+49.8^\circ$ obtained by Montgolfier (Abstr., 1878, 891). From 36 grams of borneol, 26.5 grains of crude campholic acid, 1.16 grams of isocampholic acid, 3.30 grams of borneol, and some neutral oily products are obtained.

E. H.

Compounds of the Citronella Series. CARL D. HARRIES and ALFRED HIMMELMANN (*Ber.*, 1908, 41, 2187—2199. Compare this vol., i, 714).—An investigation of the ozonides of citronellaldehyde, citronellol, and citronellic acid. These compounds decompose when treated with water, yielding acetone and β -methyladipic acid, except in the case of the ozonide of citronellol, when acetone, but not β -methyladipic acid, is obtained. The quantities obtained are 21, 32, and 52% of acetone, and 0, 35, and 58% of β -methyladipic acid respectively.

The quantities of acetone obtained closely correspond with those of β -methyladipic acid. From these results, the authors consider it highly probable that compounds of the citronella series which have hitherto been regarded as simple substances are mixtures of compounds of the citronella series, $\text{CH}_3\cdot\text{CMe}\cdot[\text{CH}_2]_3\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{R}$, with those of the isomeric rhodina series, $\text{CMe}_2\cdot\text{CH}\cdot[\text{CH}_2]_2\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{R}$. For example, ordinary citronellaldehyde is probably a mixture of a compound having the formula assigned by Barbier (Abstr., 1897, i, 537) and Harries (Abstr., 1901, i, 730) to citronellaldehyde, namely, $\text{CH}_3\cdot\text{CMe}\cdot[\text{CH}_2]_3\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CHO}$, with a substance having the constitution assigned by Bouveault (Abstr., 1900, i, 452) to the aldehyde derived from rhodinol, namely,



the latter formula was originally given by Tiemann and Schmidt to citronellaldehyde (Abstr., 1897, i, 198). From the quantities of acetone obtained from the various ozonides, it follows that ordinary citronellol contains about 20% of rhodinol, citronellaldehyde about 40% of rhodinolaldehyde, whilst citronellic acid contains about 60% of rhodinic acid.

The ketonic substances which would result from the ozonides of the citronella series ($\text{CH}_3\cdot\text{CMe}\cdot\text{CH}_2\cdot\cdot\cdot$) on treatment with water, namely, $\text{X}\cdot\text{CH}_2\cdot\text{OH}$ from citronellol, $\text{X}\cdot\text{CHO}$ from citronellaldehyde, and $\text{X}\cdot\text{CO}_2\text{H}$ from citronellic acid, where $\text{X} = \text{Me}\cdot\text{CO}\cdot[\text{CH}_2]_2\cdot\text{CHMe}\cdot\text{CH}_2\cdot$, were not isolated.

This assumption explains why Tiemann and Schmidt (*loc. cit.*) obtained only 50% of isopulegol on treating the aldehyde with acetic anhydride, and why only one-half of the citronellaldimethylacetal when oxidised with potassium permanganate is converted into the dimethylseiacetal of β -methyladipic acid (Harries and Schauwecker, Abstr., 1901, i, 448).

The compound obtained by acting on citronellaldehyde with ozone is an *ozonide peroxide*, $\text{C}_{10}\text{H}_{18}\text{O}_8$ (compare Langheld, Abstr., 1906, i, 226); it is converted by sodium hydrogen carbonate solution into the normal *ozonide*, $\text{C}_{10}\text{H}_{18}\text{O}_7$. The *ozonide*, $\text{C}_{10}\text{H}_{18}\text{O}_6$, obtained by passing

ozone into a solution of the aldehyde in carbon tetrachloride, is a non-explosive, colourless, syrupy liquid with an unpleasant odour.

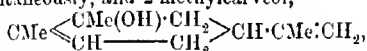
An *ozonide peroxide* of citronellic acid, $C_{10}H_{18}O_6$, is formed when ozone is passed into a solution of the acid in carbon tetrachloride until the solution no longer decolorises a solution of bromine in acetic acid. It is a slightly explosive, colourless, viscid liquid, which, when treated with water, yields an *ozonide*, $C_{10}H_{18}O_5$. An *ozonide*, $C_{10}H_{18}O_7$, is obtained by passing ozone into the solution in carbon tetrachloride until the latter becomes blue; it is similar in properties to the ozonide peroxide. An *ozonide* of citronellol, $C_{10}H_{20}O_6$, is obtained by passing ozone into a solution of citronellol in carbon tetrachloride; it is a non-explosive, colourless, viscid liquid.

W. H. G.

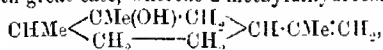
A Hydrocarbon from *isopulegone*. HANS RUPE and A. EBERT (*Ber.*, 1908, 41, 2067—2071).—The action of magnesium methyl iodide on *isopulegone* leads to the formation of a tertiary alcohol which loses water with moderate ease. It has been found previously (*Abstr.*, 1906, i, 374; this vol., i, 433, 556) that the stability of tertiary alcohols of this series depends on the relative position in the molecule of the carbinol group and an ethylene linking, the loss of water taking place the more readily the nearer these are together.

Thus 3-methylpulegol, $CHMe \begin{smallmatrix} \text{CH}_2 \cdot CMe(OH) \\ \text{CH}_2 \text{---} CH_2 \end{smallmatrix} > CPr^3$, and 2-methyl-

carvenol, $CHMe \begin{smallmatrix} CMe(OH) \cdot CH \\ \text{CH}_2 \text{---} CH_2 \end{smallmatrix} > CPr^3$, cannot be isolated, as they lose water spontaneously, and 2-methylcarvenol,



loses water with great ease, whereas 2-methyldihydrocarvenol,



and homothujyl alcohol, $CHMe \begin{smallmatrix} CMe(OH) \cdot CH_2 \\ CH \text{---} CH_2 \end{smallmatrix} > CPr^3$, which does not contain an ethylene linking, are stable, and lose water only with great difficulty. Hence it is considered that the new tertiary alcohol is

3-methylisopulegol, $CHMe \begin{smallmatrix} CH_2 \cdot CMe(OH) \\ CH_2 \text{---} CH_2 \end{smallmatrix} > CH \cdot CMe \cdot CH_2$. The

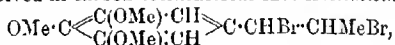
hydrocarbon formed from this by loss of water must be 3-methyl- $\Delta^{2,9}$ -menthadiene, $CHMe \begin{smallmatrix} CH \cdot CMe \\ CH_2 \cdot CH_2 \end{smallmatrix} > CH \cdot CMe \cdot CH_2$, as the molecular refraction approximates closely to the calculated, which excludes the possibility of the presence of conjugated ethylene linkings. The substances described may, however, be mixtures of isomerides (compare Wallach, this vol., i, 402).

3-Methylisopulegol, $C_{11}H_{20}O$, is a mobile oil, b. p. 93—94° 12 mm., D_4^{20} 0.9108, n_D^{20} 1.4699, $[\alpha]_D^{20}$ 19.54°, has an odour resembling geraniol, and, on treatment with phosphorus trichloride in ethereal solution, yields 3-chloro-3-methyl- $\Delta^{8(6)}$ -menthene, $C_{11}H_{18}Cl$, which is obtained as a mobile, colourless oil, b. p. 92—93°/10 mm., gradually decomposing at the ordinary temperature.

• 3-Methyl- $\Delta^{2(9)}$ -menthadiene, $C_{11}H_{18}$, prepared by heating the preceding chloro-compound with potassium acetate in alcoholic solution, or by converting the tertiary alcohol into its *acetyl* derivative and distilling this under the ordinary pressure and again over sodium, forms a mobile liquid having a slight odour of menthene. Of the following physical constants, the first series is those obtained with the hydrocarbon prepared from the chloro-compound, and the second with that from the acetyl derivative, b. p. 180—185°/750 mm. or 95—97°/12 mm., D^{20}_D 0.8401, n^{20}_D 1.4734, $[\alpha]^{20}_D + 29.00^\circ$; b. p. 182—184°/750 mm. or 95—97°/12 mm., D^{20}_D 0.8400, n^{20}_D 1.4724, $[\alpha]^{20}_D + 46.27^\circ$.

G. Y.

Components of Ethereal Oils. Establishment of the Constitutional Formulæ of Elemicin and *iso*Elemicin. FRIEDRICH W. SEMMLER (*Ber.*, 1908, 41, 2183—2187).—Elemicin (compare this vol., i, 557) is definitely shown to be 3:4:5-trimethoxy-1-allylbenzene; *iso*elemicin is therefore 3:4:5-trimethoxy-1-propenylbenzene. Elemicin, obtained by fractional distillation from the ethereal oil, has been further purified by treatment with concentrated formic acid; it then has b. p. 144—147°/10 mm., D^{20}_D 1.063, n_D 1.52848. *iso*Elemicin, obtained from elemicin purified in this manner, has b. p. 153—156°/10 mm., D^{20}_D 1.073, n_D 1.54679. It is converted by bromine dissolved in carbon tetrachloride into *isoelemicin dibromide*,



forming crystals, m. p. 89—90°.

W. H. G.

Preparation of Santalyl Camphorate. J. D. RIEDEL (D.R.-P. 193960).—*Santalyl camphorate*, yellow oil, D 0.9945/24°, is produced by heating methyl camphorate with 2 to 4 parts of santalol, or the corresponding amount of sandal-wood oil at 150—200° for several hours. The excess of santalol, or oil, is expelled in steam, and the new ester is obtained from the residue.

G. T. M.

Reduction of Aliphatic Terpene Compounds. C. J. ENKLAAR (*Ber.*, 1908, 41, 2083—2087).— $\beta\zeta$ -Dimethyloctane (Willstätter and Mayer, this vol., i, 383) is obtained by reduction of ocimene (van Romburgh, *Abstr.*, 1901, i, 220), geraniol, or linalool with hydrogen in presence of nickel at 130°. When reduced with sodium and alcohol, and thereafter treated with bromine, ocimene and myrcene yield the same *dihydro ocimene tetrabromide*, m. p. 88°. Hence ocimene, *allo*-ocimene, and myrcene are derivatives of the same decane. A comparison of the properties of $\beta\zeta$ -dimethyloctane obtained with those of Willstätter and Mayer's preparation shows that, whilst ocimene does not contain cyclic terpenes, myrcene cannot be freed from these.

Reduction of geraniol with limited amounts of hydrogen leads to the formation of decanol (Willstätter and Mayer, *loc. cit.*), together with a cyclic alcohol, $C_{10}H_{20}O$, D^{15}_D 0.906, which yields a *phthalate*, m. p. 169—170°, and is therefore not identical with *r*-menthol or thymomenthol, and considerable amounts of a *product*, $C_{31}H_{52}O$, b. p. 192—194°/22 mm., D^{17}_D 0.8500, n^{19}_D 1.4564.

G. Y.

Phellandrene from Water Fennel Oil. IWAN L. KONDAKOFF (*J. pr. Chem.*, 1908, [ii], 78, 42—46).—It has been shown previously that the so-called natural phellandrene, obtained from water fennel oil, consists of a mixture of a phellandrene and at least 20% of pinene, which, on treatment with hydrogen chloride, forms *d*-bornyl chloride, dipentene dihydrochloride, and a mixture of liquid hydrochlorides. These when treated with alcoholic potassium hydroxide yield Kindt's camphor and a hydrocarbon containing small amounts of dipentene (Abstr., 1907, i, 329, 712, 713). These various products have now been further investigated. It is found that, on treatment with hydrogen chloride in various solvents, natural phellandrene yields *d*-bornyl chloride, with or without small amounts of dipentene dihydrochloride, formed from pinene, and an unsaturated monohydrochloride, sometimes together with a stable, liquid dihydrochloride, formed from the phellandrene. An optically inactive hydrocarbon, b. p. 177—182°, D^{20}_D 0.848, n_D 1.47877, containing possibly traces of camphene and dipentene, is obtained from the monohydrochloride and from the stable dihydrochloride. This hydrocarbon resinifies rapidly on exposure to air, and forms a liquid nitrite, liquid bromide, and liquid dihydrochloride. As the hydrochlorides of pinene have smaller rotatory powers than the hydrocarbon, and as natural phellandrene yields bornyl chloride with $[\alpha]^{25}_D + 28.3^\circ$, the pinene contained in natural phellandrene must have a rotatory power not less than 35° , whilst the hydrocarbon, ψ - or β -phellandrene, must boil above 173° , have a density less than 0.858, and be optically inactive. The constitutions of α - and β -phellandrene remain to be determined.

G. Y.

Ethereal Oils. HEINRICH HAENSEL (*Chem. Zentr.*, 1908, i, 1837; from *Geschäftsber.*, October, 1907, March, 1908).—*Acaroid resin oil* is reddish brown in colour, and in odour resembles tolu- and peru-balsam, D^{20}_D 0.9600, $\alpha_D \pm 0^\circ$, acid number 4.7, ester number 37.5. *Birch-leaf oil*, yellow in colour and solid at the ordinary temperature, D^{20}_D 0.8683, acid number 30, ester number 81, and from which a paraffin was obtained crystallising in leaflets, m. p. 49—50°. *Coriander oil* free from terpene has D^{15}_D 0.8786, $\alpha_D + 9.5^\circ$, ester number 13.3. *Oil of Cubebs*, obtained from cubeben, D 0.941, $\alpha_D - 13.55^\circ$. *Guaiacum resin oil* is a dark brown, aromatic-smelling oil, which is not completely soluble in 96% alcohol, D^{15}_D 0.9417, acid number 77, ester number 138, and when warmed with ammoniacal silver solution gives a silver mirror. *Rock-rose oil*, obtained from the dried plant, is dark brown and has an unpleasant odour, D^{21}_D 0.9296, acid number 0, ester number 111; it contains neither aldehyde nor ketone. *Laurel-leaf oil* has D 0.9361, $\alpha_D - 15.95^\circ$, and, besides *l*-pinene, probably contains some phellandrene. *Celandine oil*, from the dry plant, is brown and has a pleasant odour; it solidifies at 30° , and has D^{10}_D 0.9374. *Oil of Frankincense*, $D^{17.5}_D$ 0.8810, $\alpha_D + 22.08^\circ$, acid number 2, ester number 15.5, contains an alcohol, $C_{28}H_{44}O$. *Olibanum*, which is a thick, yellow oil, b. p. 205—212°, D^{20}_D 0.9570, $\alpha_D - 65.05^\circ$.

J. V. E.

• **Ethereal Oils.** SCHIMMEL & Co. (*Chem. Zentr.*, 1908, i, 1838—1840; from *Geschäftsber.*, April 1908. Compare Abstr., 1907, i, 782—783).—Ayapana oil has D^{15} 0.9806, $\alpha_D + 2.92^\circ$, acid number 5.5, ester number 5.9; the yield of this oil from the leaves of *Eupatorium triplinervia* from Ceylon, 1.14%. A fraction obtained from camphor oil, b. p. 175.5—177°/763 mm., D^{15} 0.8470, $\alpha_D + 33.77^\circ$, contained a considerable quantity of *d*-limonene with dipentene. Oil of lemon from Java may occasionally be dextrorotatory up to $+1.77^\circ$; an oil not differing in properties from Java oil of lemon had D^{15} 0.9058, $\alpha_D + 0.17^\circ$, a total content of 79.7% ($C_{10}H_{18}O$), and was soluble in 1 vol. 80% alcohol. Oil of bergamot from Ischia Island does not differ from the ordinary commercial oil from Messina; it is brownish-green in colour and strong smelling, D^{15} 0.8828, $\alpha_D + 1.3^\circ$, acid number 1.8, ester number 96.4, and corresponds with 33.7% linalyl acetate; non-volatile residue, 5.2%. A small quantity of oil (yield, 2.94%) distilled from the seeds of *Heracleum giganteum* had the following constants: D^{15} 0.8738, $\alpha_D + 1^\circ$, n_D^{20} 1.42102, acid number 3.7, ester number 281.9, after acetylation 311.8, and dissolved in 1.2 vols. 80% alcohol. Kobuschi oil from the young twigs and leaves of *Magnolia Kobus* had D^{15} 0.9451, $\alpha_D - 1.5^\circ$, acid number 0.7, ester number 4.3, and contained citral and cineol together with about 16% anethole and probably also methylchavicol.

Oil from *Lavandula stoechas* contains *d*-fenchone and *d*-camphor. A sample of *Niaouli* oil (from *Melaleuca viridiflora*) obtained from New Caledonia was pale lemon-yellow in colour, smelling strongly like eucalyptol, and had D^{15} 0.9284, $\alpha_D - 1.17^\circ$; it contained about 40% cineol. Oil of Savin does not contain pinene, thus enabling any adulteration with turpentine oil to be detected.

Canadian Snakeroot oil, from the air-dried disintegrated root of *Asarum canadense* (Indian ginger root, wild ginger), yields 3.36% of a yellowish-brown aromatic oil, D^{15} 0.9508, $\alpha_D - 22^\circ$, n_D^{20} 1.48537, acid number 3.7, ester number 115.9, after acetylation 140.1, soluble in 2.7 vols. and more of 70% alcohol. The oil obtained from the root without the fibre (yield, 3.83%) is purer yellow in colour, and has D^{15} 0.9516, $\alpha_D - 2.83^\circ$, n_D^{20} 1.48508, acid number 3.7, ester number 117.6, after acetylation 137.2, and it dissolves in 2.3 vols. 70% alcohol. The oil from the fibre of the root (yield, 1.20%) had D^{15} 0.9659, $\alpha_D - 39.66^\circ$, n_D^{20} 1.50280, acid number 2.2, ester number 39.2, after acetylation 110.2, and is not soluble in 10 vols. 70% alcohol, but soluble in 0.9 vols. 80% alcohol.

The residue obtained from the purification of American turpentine oil gives, when fractionated, portions which are rich in β -pinene, especially the fraction, b. p. 164—166°.

American Wormseed oil (from *Chinopodium ambrosioides* var. *anthelminticum*) has D 0.96—0.98, and dissolves in 10 vols. 70% alcohol to a clear solution; oils have, however, for some time been met with having D 0.93—0.95, which are only soluble in 80% alcohol, the difference in properties being caused by a slow distillation process. It is advised to distil at a moderate rate and to employ only the seeds of the plant; the plant free from seeds gives no oil. A careful investigation of this oil showed D^{15} 0.9768, $\alpha_D - 4.5^\circ$, n_D^{20} 1.47850, acid number

0, saponification number 8.4, after acetylation 280.1, and it was soluble in 4 vols. 70% alcohol. The acetylated oil was heavier than water, and had a strong scent similar to spearmint. Small quantities of a terpene, probably silvestrene, *p*-cymene, and also *d*-camphor have been found in the oil; the chief constituent, however, is a repugnant-smelling substance, *ascaridol*, $C_{10}H_{16}O_2$, b. p. $83^{\circ}/4-5$ mm., D^{15}_D 1.0079, n_D^{20} 1.47431. Towards reagents which show alcoholic, aldehydic, ketonic, or phenolic characters, this substance is quite indifferent only with 50% resorcinol solution does it give, at the ordinary temperature, an unstable liquid compound, which when heated to $130-150^{\circ}$ decomposes with explosive violence. It appears that at 150° a transformation takes place; the product purified by vacuum distillation had b. p. $98.5-99.5^{\circ}/4.5$ mm., D^{15}_D 1.0266, n_D^{20} 1.46515, and had a similar composition to that given above. Ascaridol reacts violently with concentrated formic acid, giving cymene, but less readily with alcohol, potassium hydroxide, or zinc chloride; zinc dust and acetic acid give cymene and probably also carvenone. Oxidation with potassium permanganate (1% solution) gives an acid mixture in which, besides formic, acetic, and isobutyric acids, a higher boiling liquid acid is obtained ($C_{10}H_{16}O_4$), b. p. $80-81^{\circ}/5$ mm., D^{15}_D 1.0641, n_D^{20} 1.44388, which when heated to $120-130^{\circ}$ gives methylheptenone. The transformation product of ascaridol decomposes when boiled with water, and gives with zinc dust and acetic or formic acid no cymene, but with the latter a ketone, $C_{10}H_{14}O$, semicarbazone, m. p. $194-195^{\circ}$. Normal American oil (D^{15}_D 0.9708) contains 62-65% of ascaridol and about 22% of cymene, but light oil (D^{15}_D 0.9426), only 45-50% of ascaridol.

Hyssop oil, from dried flowering plants, had D^{15}_D 0.9377, n_D^{20} 1.4650, acid number 1.8, ester number 5.8, after acetylation 44, and is soluble in about 6 vols. 80% alcohol with separation of paraffin. From withered flowering plants, the oil had D^{15}_D 0.9322, n_D^{20} 1.4640, acid number 1.3, ester number 3.6, after acetylation 37.3, n_D^{20} 1.48315, and is soluble in about 8 vols. 80% alcohol with separation of paraffin. Very faded flowering plants yielded an oil, D^{15}_D 0.9336, n_D^{20} 1.48141, acid number 1.8, ester number 3.1, and is soluble in about 7 vols. 80% alcohol with separation of paraffin; the last oil appears to contain β -pinene, *L*-pinocamphone, and a very small quantity of an alcohol, b. p. $221-222^{\circ}$. The higher boiling portions of this oil are probably sesquiterpenes. A beautiful crystalline *dibromide* has been obtained from *L*-pinocamphone, m. p. $93-94^{\circ}$, which gives in alcohol solutions an alcohol of camphor-like odour, m. p. $67-68^{\circ}$, b. p. $217-218^{\circ}$. When reduced or oxidised, it yields *l*-pinonic acid, $C_{10}H_{16}O_3$, m. p. $69.5-70.5^{\circ}$, but when oxidised by sulphuric acid, *l*-menthoethylheptanonolide, m. p. $46-47^{\circ}$, is produced.

The following oils from Mayotte are described for the first time: Two *Basilicum* oils, one of which contains eugenole, whilst the other, from *B. canum* (*Ocimum canum*), contains a considerable quantity of *d*-camphor; also an oil from Mexico from the leaves of *Schinus molle*, a colourless oil, D^{15}_D 0.8583, n_D^{20} 1.4483, ester number 7.2; that from the fruit was pale yellow, D^{15}_D 0.8600, n_D^{20} 1.4252, ester number 25.2, after acetylation 56.5; both these oils give strong phellandrene reactions.

Oil from the leaves and flowers of *Buddleia perfoliata* from Mexico: a pleasant, although peculiar, smelling pale yellow oil, D_{20}^{25} 0.8862, n_D^{25} — 25°, acid number 0.6, ester number 8.1.

Oil from *Vitex agnus castus*.—The leaves of this plant give 0.48% of a brown oil, which has an odour resembling hyssop, D_{20}^{25} 0.9010, n_D^{25} 7.92°, acid number 6.4, ester number 18.3, after acetylation 58.4; it contained cineol and probably sabinene.

J. V. E.

Transformations of Chlorophyll under the Influence of Acids. LAD. HULT, LEON MARCHLEWSKI, and J. ROBEL (*Bull. Acad. Sci. Cracow*, 1908, 261—296. Compare Willstätter and Hocheder. Abstr., 1907, i, 784).—The conclusion is drawn that chlorophyllan, phaeophytin, and phyllogen are identical. The two last are obtained by the action of acids on chlorophyll at low temperatures and as a rule contain no phylloeyanin or other decomposition product which is not extracted from the ethereal solution by 15% hydrochloric acid. Phaeophytins containing strongly basic products have been obtained, for example, from *Acacia* leaves. Chlorophyllan is usually obtained at higher temperatures, and can therefore contain decomposition products, but phyllogens have been prepared which react with 15% hydrochloric acid in exactly the same manner as chlorophyllans, and thus the chief difference between the two groups is removed.

J. J. S.

Conversion of Phyllotaonin into Phytorhodins. T. KOZNIEMSKI and LEON MARCHLEWSKI (*Bull. Acad. Sci. Cracow*, 1908, 247—261; *Biochem. Zeitsch.*, 1908, 10, 472—485).—It is shown by means of spectroscopic measurements that *allo*phyllotaonin is converted, under the influence of acids at high temperatures, into substances which are identical with Willstätter and Mieg's phytorhodins (Abstr., 1907, i, 69). The conversion of alkachlorophyll into these compounds thus takes place in two stages, the intermediate product being *allo*phyllotaonin. Phyllotaonin and *allo*phyllotaonin are much more closely related to alkachlorophyll than are the phytorhodins.

A very marked difference exists in the behaviour of phyllotaonin and the phytorhodins towards alkalis at high temperatures. Phyllotaonin is the best source for the preparation of phylloporphyrin, whereas phytorhodins do not yield this compound when heated with alkali at 200° under pressure.

J. J. S.

Phaeophytin and Chlorophyllan with some Concluding Remarks on Phylloxanthin. M. TSVETT (*Biochem. Zeitsch.*, 1908, 10, 404—413).—The dark green precipitate which is formed from chlorophyll solutions by the addition of organic acids or of traces of hydrochloric acid (Tschirsch's chlorophyllan, Willstätter's phaeophytin) is a mixture of the immediate products formed by the action of acid on chlorophyll, that is, a mixture, according to the author, of the already described α - and β -chlorophyllans; at any rate, it can by the absorption-analysis method be separated into constituents with the same spectroscopic properties and chemical reactions. By throwing it into Frémy's diphasic ethyl ether hydrochloric acid mixture, it gives the so-called phylloxanthin, which is apparently unchanged

β -chlorophyllan and remains in ethereal solution, and the so-called phyllocyanin, which is not unchanged α -chlorophyllan, but a mixture that can be resolved into its components by Willstätter's method of acid fractionation. S. B. S.

The Nature of the So-called Crystallisable Chlorophyll ("Metachlorophyllin"). M. TSVETT (*Biochem. Zeitsch.*, 1908, 10, 414—425).—The so-called "crystallisable chlorophyll" (α -metachlorophyllin) is not a natural constituent of chlorophyll, but an artifact, which is formed by the slow extraction of plants, and is formed from the genuine chlorophyllin under the influence of some unknown factor in the cell mechanism. Chlorophyll extracts immediately after preparation are free from this substance. In its spectrum, it combines the bands of both chlorophyllins (α and β), and must be considered as derived from both. S. B. S.

A New System of the So-called Chlorophyll Derivatives. M. TSVETT (*Biochem. Zeitsch.*, 1908, 10, 426—429).—According to this system there are two main constituents of chlorophyll extract, namely, α -chlorophyllin and β -chlorophyllin. By the action of alkalis at low temperatures they yield respectively α - and β -chlorophyllic acids. The former of these, on treatment with alkali at 200°, yields Willstätter's rhodophyllin (from which by the action of acids alloporphyrin is obtained), whereas the latter under the same conditions yields phylloporphyrin. On treatment with weak acids, α -chlorophyllin yields chlorophyllan, from which, by the action of strong acids, Schunck's phyllocyanin is obtained. This on further treatment by acid, yields Willstätter's phytochlorins and phytorhodins. β -Chlorophyllin, on treatment with weak acids, yields β -chlorophyllan (Tschirch and Schunck's phylloxanthin), from which by more energetic hydrolysis the phytochlorins and phytorhodins are obtainable. These latter substances are obtainable directly from chlorophyllic acid by energetic hydrolysis. S. B. S.

Theory of Mordant Dyes. LEO A. TSCHUGAEFF (*Ber.*, 1908, 41, 2245—2246).—Polemical. A reply to Liebermann (this vol., i, 441). W. R.

Theory of Mordant Dyes. ALFRED WERNER (*Ber.*, 1908, 41, 2383—2386).—A reply to Liebermann (this vol., i, 441). G. Y.

Blue Erythrosin Silver. LÜPPO-CRAMER (*Zeitsch. Chem., Ind. Kolloide*, 1908, ii, 325—326).—When silver nitrate is added to an excess of a dilute solution of erythrosin, a much more intensely coloured colloidal solution of the silver salt of erythrosin is obtained. The colour of the colloidal solution is distinctly more blue than the original. On boiling or on keeping for some time, the solution becomes opalescent, and the erythrosin silver compound, which has a pure blue colour, gradually separates.

The same thing can be observed in the presence of silver bromide or

chloride, which act as protective colloids. The separated erythrosin silver compound when shaken up with water forms a very fine suspension, which can be filtered through paper without leaving a residue.

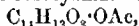
Fluorescein, dibromofluorescein, eosin, and tetraiododichlorofluorescein behave differently from erythrosin; the colloidal solutions of the silver salts in presence of colloidal silver bromide appear to be quite stable.

H. M. D.

Rosocyanin. LATHAM CLARKE and C. LORING JACKSON (*Amer. Chem. J.*, 1908, 39, 696—719).—Rosocyanin, the red colouring matter produced in the well-known test for boric acid with turmeric paper, has been studied by Schlumberger (*Bull. Soc. chim.*, 1866, [ii], 5, 194) and by Ivanow-Gajewski (this Journ., 1873, 504, 760).

In the present investigation, the rosocyanin was prepared by heating an alcoholic solution of curcumin with boric and sulphuric acids, and was obtained as a purple powder with a yellowish-green metallic lustre. It does not melt, but decomposes at 200—230°. The statement of Schlumberger and Ivanow-Gajewski that the substance does not contain boron is confirmed. Rosocyanin has the composition $C_{14}H_{14}O_4$, and is thus isomeric with curcumin. It yields only mono-salts with the alkalis, whereas curcumin gives both mono- and di-salts. It is evident, therefore, that the former substance only contains one hydroxyl group. The ammonium, potassium, and barium salts are blue. The acetyl derivative forms a brownish-red powder. The methyl ether is obtained as a purple powder resembling rosocyanin itself.

When a mixture of curcumin, boric acid, and alcohol is left for eight hours, a red solution is obtained, from which ether precipitates a red powder, which is decomposed by water into rubrocurcumin and boric acid. If a mixture of curcumin, boric acid, and alcohol in certain proportions is left for some hours and then poured into water, rubrocurcumin, $C_{14}H_{14}O_4$, is obtained as a vermilion-coloured powder; it is unstable, gradually changing into curcumin, and, when heated at 200—240°, is converted into rosocyanin. Acetyl rubrocurcumin,



m. p. 245°, forms orange-yellow, prismatic needles.

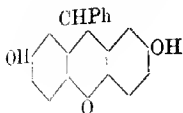
Curcumin methyl ether, $C_{15}H_{15}(OMe)_2 \cdot C_2H_5O_2$, m. p. 145°, forms small, orange-yellow needles, and, on oxidation with potassium permanganate, yields veratric acid.

Protocurcumin, $C_{15}H_{15}(OH)_2 \cdot C_2H_5O_2$, formed by the removal of a methyl group from curcumin, gives a crimson coloration when treated with boric acid, sulphuric acid, and alcohol, which is turned blue by alkali hydroxides. This substance will be described in a future paper.

E. G.

Condensation Products of Quinol. RICHARD MEYER and KARL WITTE (*Ber.*, 1908, 41, 2453—2459).—A condensation product differing from that described by Schorygin (*Abstr.*, 1907, 5, 1031) is obtained by adding small quantities of benzaldehyde to a solution of quinol in dilute sulphuric acid. From its chemical behaviour and

from the results of analysis and mol.-wt. determinations, the compound so formed is evidently 2:7-dihydroxyphenylxanthen, annexed formula.



It crystallises in glittering, slender, colourless needles, m. p. 259° (decomp.); the *acetate*, $C_{19}H_{12}O(OAc)_2$, crystallises in glistening, slender, white needles, m. p. 200° (decomp.); the *benzoate*, $C_{19}H_{12}O(OBz)_2$, forms slender needles, m. p. 237°; the *dimethyl ether*, $C_{19}H_{12}O(OMe)_2$, forms small, colourless crystals, m. p. 132°; the *diethyl ether*, $C_{19}H_{12}O(OEt)_2$, crystallises in slender, white needles, m. p. 100—101°; the *dibenzyl ether*, $C_{19}H_{12}O(O\cdot CH_2Ph)_2$, forms stellate groups of small needles, m. p. 190°.

The acetate is oxidised by chromic acid, yielding the *carbinol*, $O\langle \begin{smallmatrix} C_6H_5(OAc) \\ C_6H_5(OAc) \end{smallmatrix} \rangle CPh\cdot OH$, m. p. 171—172°; the corresponding *benzoate*, $C_{19}H_{12}O_2(OBz)_2$, has m. p. 209°.

Condensation products of quinol with formaldehyde, acetaldehyde, chloral, &c., could not be isolated in a pure state.

Succinic anhydride (1 mol.) when heated with quinol (2 mols.) yields a *succinein*, $CO\langle \begin{smallmatrix} C_6H_5 \\ O \end{smallmatrix} \rangle C\langle \begin{smallmatrix} C_6H_5(OH)_2 \\ C_6H_5(OH)_2 \end{smallmatrix} \rangle$; it crystallises in slender, white needles, m. p. 217°. The *acetate*, $C_{19}H_{12}O_2(OAc)_2$, forms small, white crystals, m. p. 161—162°. The corresponding benzoate could not be obtained; in all cases, quinol dibenzoate was formed. Attempts to prepare the dihydroxy-compound corresponding with the acetate were also unsuccessful.

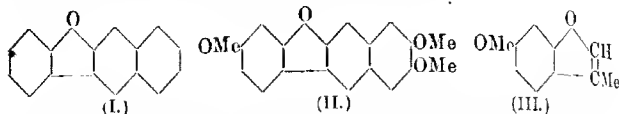
W. H. G.

Pyronone Syntheses by means of the "Tertiary Bases Reaction." I. EDGAR WEDEKIND and JOHANNES HAEUSSERMANN (*Ber.*, 1908, 41, 2297—2302).—The term "tertiary bases reaction" is used to denote the condensation of acyl halides by means of tertiary bases, a reaction which led to the production of dehydracetic acid from acetyl chloride (Wedekind, *Abstr.*, 1902, i, 739, compare also Wedekind and Weisswange, *Abstr.*, 1906, i, 437). The authors have now studied the action of tripropylamine on propionyl chloride, and have obtained a product the molecular weight of which is three times that of monomethylketen (which may be formed as an intermediate compound, compare Staudinger and Klover, this vol., i, 318), but it is not identical with trimethylphloroglucinol. The substance is probably formed by loss of 2HCl from 3 mols. of propionyl chloride, forming the compound $COEt\cdot CHMe\cdot CO\cdot CHMe\cdot COCl$, which is partly transformed into the enolic modification, and loses hydrogen chloride, thus: $CO\langle \begin{smallmatrix} CHMe\cdot COCl \\ CMe\cdot CEt\cdot OH \end{smallmatrix} \rangle \rightarrow CO\langle \begin{smallmatrix} CHMe\cdot CO \\ CMe\cdot CEt \end{smallmatrix} \rangle O$, giving 3:5-dimethyl-2-ethyl-4:6-pyronone. This separates from glacial acetic acid in monoclinic crystals, m. p. 151°. On heating with alkalis under pressure, it is decomposed into propionic acid and diethyl ketone, and an acetic acid solution absorbs bromine.

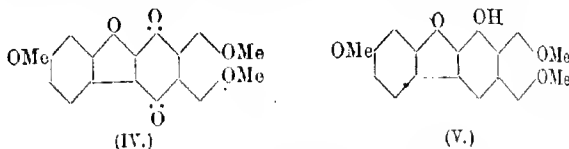
J. C. C.

Brazen from Naphthalene STANISLAUS VON KOSTANECKI and VICTOR LAMPE (*Ber.*, 1908, 41, 2373—2377).—The constitution (I)

for brazan suggested by Kostanecki and Lloyd (Abstr., 1903, i, 645) is supported by the following facts: (1) Those transformation products which in the brazilin series yield brazan, in the haematoxylin series form naphthalene. (2) 2:7:8-Trimethoxybrazan (II) behaves towards concentrated sulphuric acid in the same manner as its analogue, 5-methoxy-2-methylcoumarone (III).

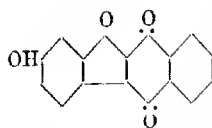


(3) 2:7:8-Trimethoxybrazanquinone (IV), obtained from 5- or 10-hydroxy-2:7:8-trimethoxybrazan (V), behaves as a *p*-quinone.



Hence, brazan contains a naphthalene and a coumarone nucleus, and is a $\beta\beta$ -derivative of naphthalene. The constitution of brazan has now been confirmed by syntheses.

Liebermann (Abstr., 1899, i, 523) prepared anhydro- α -naphthaquinonesoreinol (2-hydroxybrazanquinone, annexed formula)

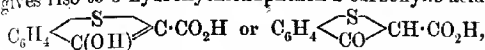


from 2:3-dichloro- α -naphthaquinone. The 2-hydroxy-compound crystallises in orange-yellow needles, m. p. 320°, gives a bluish-green coloration with concentrated sulphuric acid, and is converted by methyl sulphate and alkalis into 2-methoxybrazanquinone, $C_{17}H_{10}O_4$, crystallising in golden leaflets, m. p. 290°. This resembles 2:7:8-trimethoxybrazan in that it distils unchanged when carefully heated and behaves like the hydroxy-compound towards concentrated sulphuric acid. When heated with hydriodic acid, 2-methoxybrazanquinone yields 2-hydroxybrazan, $C_{16}H_{10}O_2$, which forms white crystals, m. p. 255°, gives a green coloration with alcoholic ferric chloride, and dissolves in sodium hydroxide to a colourless solution with blue fluorescence. 2-Acetoxybrazan, $C_{18}H_{12}O_3$, white needles, m. p. 196—197°, has a slight blue fluorescence in alcoholic solution. 2-Methoxybrazan, $C_{17}H_{12}O_3$, prepared by the action of methyl sulphate and alkalis on the hydroxy-compound, crystallises in white leaflets, m. p. 205—206°, and gives colorations with ferric chloride and sulphuric acid. Brazan, m. p. 202°, is obtained when 2-hydroxybrazan or 2-hydroxybrazanquinone is distilled with zinc dust.

G. Y.

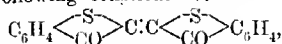
Preparation of a Red Colouring Matter of the Thionaphthen Series. KALLE & CO. (D.R.-P. 194237 and 194254).—Phenylthioglycol- α -carboxylic acid, when treated with condensing agents or when

heated, gives rise to 3-hydroxythionaphthen-2-carboxylic acid,



and 3-hydroxythionaphthen, $\text{C}_6\text{H}_4 \begin{array}{c} \text{S} \\ \diagup \quad \diagdown \\ \text{C}(\text{OH}) \end{array} \text{CH}$ or $\text{C}_6\text{H}_4 \begin{array}{c} \text{S} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{CH}_2$.

When either of these compounds is oxidised with ferric chloride or potassium dichromate in the presence of alkali and the solution then acidified, a red colouring matter is precipitated. This product probably has the following constitution:



and resembles indigotin in its chemical properties; it furnishes a colourless leuco-derivative, which is again converted into the colouring matter by aerial oxidation. The red colouring matter is also produced on warming 3-hydroxythionaphthen with sulphur or by adding milk of sulphur to an alkaline solution of 3-hydroxythionaphthen-2-carboxylic acid. In the latter case, the dye is precipitated with acid.

G. T. M.

Indigoid Dyes. I. PAUL FRIEDLÄNDER (*Monatsh.*, 1908, 29, 359—374. Compare Abstr., 1906, i, 378; 1907, i, 334; this vol., i, 260, 371).—The author has prepared further members of this class of dyes (compare also following abstracts), of which a general account is given. In addition to the work previously published (compare also Bezdzik, Friedländer, and Koeniger, this vol., i, 200), the following is new. "Leucothioindigotin" (Abstr., 1907, i, 335) forms a diacetyl derivative, $\text{C}_{16}\text{H}_{18}\text{O}_2\text{S}(\text{COMe})_2$, colourless, glistening needles, m. p. 240°. "2:3-Bisthionaphthenindigotin" (thioindirubin) [2:3-bisoxylthio-

naphthen]. $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{S} \end{array} \text{C} : \text{C} \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{S} \end{array} \text{C}_6\text{H}_4$, formed by condensing hydroxythionaphthen with thionaphthenquinone in glacial acetic acid solution with addition of a little hydrochloric acid, crystallises in red needles, m. p. 205—207°.

J. C. C.

Indigoid Dyes. II. A. BEZDZIK and PAUL FRIEDLÄNDER (*Monatsh.*, 1908, 29, 375—386. Compare preceding abstract).—A detailed account of work previously published (Friedländer, this vol., i, 371, 372). The following is new:

"3-Thionaphthen-2-indole-indigotin" [2'-indoxyl-3-thionaphthen-2'-one]. $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{NH} \end{array} \text{C} : \text{C} \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{array} \text{S}$, prepared by heating indoxyl with thionaphthenquinone in glacial acetic acid solution, crystallises from xylene in violet-black needles, m. p. 247—250°, which sublime at a higher temperature.

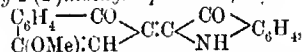
"2-Thionaphthen-3-indole-indigotin" [3'-indoxyl-2-thionaphthen-3-one]. $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{S} \end{array} \text{C} : \text{C} \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{array} \text{NH}$, prepared similarly from isatin and hydroxythionaphthen, crystallises from nitrobenzene in small, red needles, which do not melt at 270°, and sublime at a higher temperature. The dye (thioindigo-scarlet) forms a pale yellow leuco-compound,

from which textile fibres are dyed scarlet. An improved method of preparing 2'-indoxyl-3-thionaphthen-2'-one consists in condensing isatin chloride and hydroxythionaphthen in benzene solution in presence of phosphoryl chloride. It is also formed by heating together α -isatinanilide and hydroxythionaphthen either in petroleum or in acetic anhydride. 1-Oxy-2:(2')-indoxynaphthalene is best prepared by condensing α -isatinanilide with α -naphthol in acetic anhydride solution. When prepared from isatin chloride (this

vol., i, 372), an isomeric dye, $\text{CO} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CH:CH} \end{smallmatrix} \text{C}:\text{C} \begin{smallmatrix} \text{CO} \\ \text{NH} \end{smallmatrix} \text{C}_6\text{H}_4$, is also formed, which crystallises from glacial acetic acid in compact prisms, resembling potassium permanganate. It forms a brownish-yellow acetyl derivative, crystallising from glacial acetic acid in compact, glistening needles. When isatin chloride is condensed with 2-chloro- α -naphthol, a dye, $\text{CO} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CH:Cl} \end{smallmatrix} \text{C}:\text{C} \begin{smallmatrix} \text{CO} \\ \text{NH} \end{smallmatrix} \text{C}_6\text{H}_4$, is obtained, which crystallises from glacial acetic acid in brassy, dark prisms.

1-Oxy-2:(3')-indoxynaphthalene, $\text{CH} \begin{smallmatrix} \text{CH:CO} \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{C}:\text{C} \begin{smallmatrix} \text{CO} \\ \text{NH} \end{smallmatrix} \text{C}_6\text{H}_4$, prepared by condensing isatin chloride with β -naphthol in benzene solution, crystallises from xylene in blackish-violet, glistening needles.

4-Methoxy-1-oxy-2:(2')indoxynaphthalene,



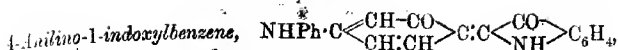
prepared by condensing 4-methoxy- α -naphthol with α -isatinanilide in acetic anhydride solution, forms bluish-black, glistening needles.

8-Oxy-7-indoxylacenaphthene, $\text{CO} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_{10}\text{H}_6 \end{smallmatrix} \text{C}:\text{C} \begin{smallmatrix} \text{CO} \\ \text{NH} \end{smallmatrix} \text{C}_6\text{H}_4$, is obtained by condensing indoxyl with acenaphthenequinone in glacial acetic acid solution. It forms coppery needles; from the leuco-compound, reddish-violet shades on textile fibres are obtained. The sulphonic acid of the dyestuff gives a reddish-violet solution in water.

8-Oxy-7-oxythionaphthenylacenaphthene, $\text{CO} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_{10}\text{H}_6 \end{smallmatrix} \text{C}:\text{C} \begin{smallmatrix} \text{CO} \\ \text{S} \end{smallmatrix} \text{C}_6\text{H}_4$, prepared by condensing hydroxythionaphthen with acenaphthenequinone in glacial acetic acid solution, crystallises from nitrobenzene in brick-red, glistening needles. By the use of the leuco-compound, textile fibres are dyed red. J. C. C.

Indigoid Dyes. III. PAUL FRIEDLÄNDER and R. SCHULOFF (*Monatsh.*, 1908, 29, 387—393. Compare preceding abstracts).—

4-Hydroxy-1-indoxylbenzene, $\text{HO} \cdot \text{C} \begin{smallmatrix} \text{CH:CO} \\ \text{CH:CH} \end{smallmatrix} \text{C}:\text{C} \begin{smallmatrix} \text{CO} \\ \text{NH} \end{smallmatrix} \text{C}_6\text{H}_4$, prepared by condensing isatin chloride with resorcinol in benzene solution, crystallises from alcohol in bronzy, dark violet needles. It forms a sulphonic acid. 4-Methoxy-1-indoxylbenzene, similarly obtained from resorcinol monomethyl ether, forms brownish-violet needles, m. p. 162°. The sulphonic acid is red. On warming with dilute sodium hydroxide the dye yields *o*-hydroxyanisaldehyde.



prepared by condensing isatin chloride with *m*-hydroxydiphenylamine in benzene solution, forms violet needles.

3-Hydroxy-1-indoxylbenzene, similarly prepared from catechol, forms violet-black needles, m. p. 245° (decomp.). It dyes iron- and chrome-mordanted cotton in greenish-blue shades. 3:4-Dihydroxy-1-indoxylbenzene, obtained from pyrogallol, forms blackish-violet needles and gives bluish-violet shades on iron- and chrome-mordanted cotton. The sulphonic acid is red. J. C. C.

Constitution of Neosine. D. ACKERMANN and FRIEDRICH KETSCHER (*Zeitsch. physiol. Chem.*, 1908, 56, 220—222).—Neosine, $\text{C}_6\text{H}_{17}\text{O}_3\text{N}$, from meat-extract, yields on distillation with baryta, trimethylamine, and is perhaps a homologue of choline. G. B.

Tropine. ERNST SCHMIDT and A. KIRCHER (*Chem. Zentr.*, 1908, i, 1467; from *Pharm. Post.*, 1907, 40, 771—772).—The authors show that the tropine bromide prepared directly from tropine is identical with α -tropidine hydrobromide, $(\text{C}_8\text{H}_{14}\text{BrN}, \text{HBr})$; it forms colourless, needle-shaped crystals, m. p. 216—217°, and gives an *aurichloride*, $(\text{C}_8\text{H}_{14}\text{BrN}, \text{HAuCl}_4)$, which crystallises in yellow needles, m. p. 170°, and a *platinichloride*, $(\text{C}_8\text{H}_{14}\text{BrN})_2 \cdot \text{H}_2\text{PtCl}_6$, which crystallises in long, red needles, blackening at 210°, and m. p. 215—216°. Silver nitrate decomposes the bromide, removing hydrogen bromide; the product gives a crystalline, anhydrous *platinichloride*, $(\text{C}_8\text{H}_{13}\text{N})_2 \cdot \text{H}_2\text{PtCl}_6$, m. p. 160—161° (decomp.), and is not identical with that obtained from tropidine. J. V. E.

Synthesis of Amino-acids. VII. Proline (Pyrrolidine-2-carboxylic Acid). SÖREN P. L. SÖRENSEN and A. C. ANDERSEN (*Zeitsch. physiol. Chem.*, 1908, 56, 236—249. Compare Abstr., 1903, i, 833; 1905, i, 600, 749; Willstätter, 1900, i, 405; Fischer, 1901, i, 745).—A good yield of pyrrolidine-2-carboxylic acid is obtained by boiling ethyl γ -bromopropylphthaliminomalonate with alcoholic sodium hydroxide and evaporating the product with hydrochloric acid. The acid is isolated and purified by means of its copper salt.

Proline is not formed when arginine is hydrolysed with barium hydroxide solution. Under suitable conditions, the amount of ornithine obtained during the hydrolysis is 64% of that required by Schultz and Winterstein's equation: $\text{NH}_2\text{C}(\text{NH}_2) \cdot \text{NH} \cdot [\text{CH}_2]_3 \cdot \text{CH}(\text{NH}_2) \cdot \text{CO}_2\text{H} + \text{H}_2\text{O} \rightarrow \text{NH}_2[\text{CH}_2]_2 \cdot \text{CH}(\text{NH}_2) \cdot \text{CO}_2\text{H} + \text{CO}(\text{NH}_2)_2$. J. J. S.

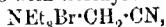
New Method of Preparing Bromoacetonitrile and its Addition to Tertiary Bases. JULIUS VON BRAUN (*Ber.*, 1908, 41, 2113—2123. Compare this vol., i, 625).—The interaction of cyanogen bromide and tertiary bases according to the equation $\text{RR}'\text{NR}'' + \text{BrCN} = \text{RR}'\text{N} \cdot \text{CN} + \text{R}''\text{Br}$, has hitherto been applied chiefly to the preparation of secondary bases (compare Abstr., 1904, i, 344, 687; this vol., i, 626, 684, and Sachs and Weigert, Abstr., 1907, i, 1046), but it also affords

a means of preparing alkyl bromides that are not readily obtained directly, provided that the tertiary base is readily accessible and has been prepared by some other method than the alkylation of a primary or secondary amine by an alkyl halide.

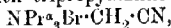
The use of dimethyl-, diethyl-, or dipropyl-aminoacetonitrile is not suitable for the ready preparation of pure bromoacetonitrile, and from his former researches (Abstr., 1907, i, 960) the author was led to employ piperidylacetonitrile, which was found to give good results. Bromoacetonitrile, being thus readily obtainable, has been employed in a number of reactions; in the present paper, its action towards tertiary aromatic amines and alkaloids is described. Whilst with tertiary aliphatic amines and cyclic bases, bromoacetonitrile yields normal additive products, with bases such as dimethylaniline it yields, for example, phenyltrimethylammonium bromide. The additive products which are formed with alkaloids, for example, atropine, codeine, strychnine, &c., although containing two new poisonous factors (quaternary character and cyanogen group), in addition to that inherent in the alkaloid, are relatively harmless.

When piperidylacetonitrile (200—300 grams) is mixed with 1 mol. of cyanogen bromide and, after twenty-four hours, heated on the water-bath, dicyanomethylpiperidinium bromide, $C_5NH_{10}(CH_2CN)_2Br$, is formed. This is extracted with ether, the ethereal solution evaporated, and the residue distilled. The fraction distilling at $50-90^\circ/15$ mm. contains the bromoacetonitrile, which can be purified by redistillation. The following homologues of piperidinoacetonitrile were prepared: *α*-Piperidyl-*n*-butyronitrile, $C_5NH_{10}CH_2CH_2CH_2CN$ (from piperidine and propaldehydecyanohydrin or propaldehyde potassium cyanide and sodium hydrogen sulphite), colourless liquid, b. p. $88-91^\circ/7$ mm. *α*-Piperidyl-*n*-hexonitrile, $C_5NH_{10}CH_2(CH_2)_4CN$ (from piperidine and valeraldehyde), colourless liquid with a weak odour of valeraldehyde, b. p. $123^\circ/12$ mm. *α*-Piperidyl-*n*-octonitrile, $C_5NH_{10}CH_2(CH_2)_6CN$ (from piperidine and heptaldehyde) is a colourless, viscous oil with a weak odour of heptaldehyde, b. p. $158-159^\circ/9$ mm. When these homologues of piperidylacetonitrile are treated with cyanogen bromide in the cold, only the hydrobromides of the compounds are formed; with water they are decomposed into the parent aldehyde, hydrogen cyanide, and piperidine hydrobromide. *α*-Piperidyl-*n*-octonitrile hydrobromide has m. p. 155° .

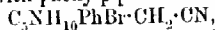
Bromoacetonitrile forms with triethylamine a compound,



m. p. 202° (decomp.), with tripropylamine a compound,



m. p. 167° (decomp.), with phenylpiperidine a compound,



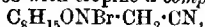
m. p. 171° , with pyridine a compound, $C_5NH_5Br \cdot CH_2 \cdot CN$, m. p. 160° ,

giving with alkalis a yellow precipitate, probably $\begin{matrix} CH_2 \cdot CH \cdot CH \cdot OH \\ | \\ CH_2 \cdot CH \cdot N \cdot CH_2 \cdot CN \end{matrix}$

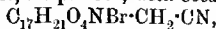
which is converted on warming into a greyish-green, amorphous powder, softening at 120° , m. p. 150° , corresponding with the composition $C_{14}H_{14}ON_4$, but which may be a mixture. With isoquinoline, bromoacetonitrile gives a compound, $C_9NH_7Br \cdot CH_2 \cdot CN$, m. p. 193° , yielding

a red precipitate with alkalis, which is at once partly converted into a reddish-yellow powder, softening at 150°, m. p. 160°.

Bromoacetonitrile gives with tropino a compound,



blackening at 215°, m. p. 225°, with atropine a very hygroscopic compound, the *platinichloride* of which, $(\text{C}_{17}\text{H}_{23}\text{O}_3\text{N}\cdot\text{CH}_2\cdot\text{CN})_2\text{PtCl}_6$, forms small, red crystals, m. p. 215°, with cocaine a compound,



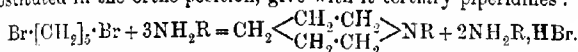
m. p. 169° (decomp.), with papaverine a compound,



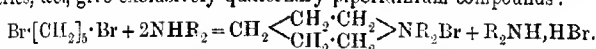
m. p. 204°, with codeine a compound, $\text{C}_{18}\text{H}_{21}\text{O}_3\text{NBr}\cdot\text{CH}_2\cdot\text{CN}$, m. p. 189°, and with strychnine a compound, $\text{C}_{21}\text{H}_{29}\text{O}_2\text{N}_2\text{Br}\cdot\text{CH}_2\cdot\text{CN}$, m. p. 273°.

J. C. C.

Characterisation of Primary, Secondary, and Tertiary Bases by the Aid of α -Dibromo-*n*-pentane. JULIUS VON BRAUN (*Ber.*, 1908, 41, 2156—2165).—The author shows that α -dibromo-*n*-pentane is an excellent agent for characterising the three classes of amines. Primary amines, in which the nitrogen is attached to an open chain, a hydrogenised carbon ring, a heterocyclic ring, or a benzene ring not substituted in the ortho-position, give with it tertiary piperidines:



When a benzene ring contains one or two ortho-substituents, pentamethylenediamino derivatives are formed (Scholtz and Wassermann, *Abstr.*, 1907, i, 339). Secondary amines of the aliphatic or piperidine series, &c., give exclusively quaternary piperidinium compounds:



In the case of secondary aromatic bases, small amounts of tertiary pentamethylenediamine bases are also formed, and when the benzene ring contains an ortho-substituent, the latter constitute the sole product.

Tertiary amines, either aliphatic or aromatic, yield diammonium bromides, $\text{Br}[\text{CH}_2]_5\cdot\text{Br} + 2\text{NR}_3 = \text{NR}_3\text{Br}\cdot[\text{CH}_2]_5\cdot\text{NR}_3\text{Br}$, but they are readily characterised only when they consist of tertiary cyclic bases, such as pyridine, methylpiperidine, &c., for the derivatives of the tertiary aliphatic amines are usually very hygroscopic, and those of the aromatic bases are formed only very slowly.

The formation of tertiary piperidines by the aid of dibromopentane has already been the subject of several investigations (compare *Abstr.*, 1904, i, 841; 1907, i, 960; *Luft, Abstr.*, 1906, i, 118; Scholtz and Wassermann, *loc. cit.*), and the author now describes *camphylpiperidine*, $\text{C}_{16}\text{H}_{17}\cdot\text{NC}_6\text{H}_5$, b. p. 134—135°/10 mm., obtained by warming 3 mols. of camphylamine and 1 mol. of dibromopentane, the excess of the base being removed by means of benzenesulphonyl chloride, whereby *camphylamine benzenesulphonate*, a red, viscid oil, is formed. *Camphylpiperidine picrate*, $\text{C}_{15}\text{H}_{27}\text{N}\cdot\text{C}_6\text{H}_5\text{O}_7\text{N}_3$, has m. p. 117°.

Diethylpiperidinium bromide, $\text{C}_5\text{NH}_{10}\text{Et}_2\text{Br}$, forms white, glistening leaflets, m. p. 257°, decomposing at this temperature into ethyl bromide

and ethylpiperidine. The *platinichloride* forms small, reddish-yellow crystals, m. p. 240°.

Diisocamylpiperidinium bromide forms silvery, hygroscopic leaflets, m. p. 115°; the *aureichloride* has m. p. 177°, and the *platinichloride* blackens at 212° and has m. p. 216°.

With dibromopentane, methylaniline forms mostly *phenylmethylpiperidinium bromide*, $C_5NH_{10}PhMeBr$, m. p. 170°, with a small quantity of *s-diphenyldimethylpentamethylenediamine*,



m. p. 38°, b. p. 244—245°/8 mm., the *picrate* of which is described, and some phenylpiperidine. Ethylaniline gives, under the same conditions, *phenylethylpiperidinium bromide*, $C_5NH_{10}PhEtBr$, m. p. 217°, and *s-diphenyldiethylpentamethylenediamine*, $NPhEt \cdot [CH_2]_5 \cdot NPhEt$, a pale yellow, viscous liquid, b. p. 257—259°/7 mm. Methyl-o-toluidine and dibromopentane yield only *s-di-o-tolyldimethylpentamethylenediamine*, $C_6H_4Me \cdot NMe \cdot [CH_2]_5 \cdot NMe \cdot C_6H_4Me$, a viscous liquid, b. p. 229°/9 mm.; the *platinichloride* is a viscid, red oil, and the *picrate* has m. p. 184°.

From tetrahydroquinoline is obtained *s-bistetrahydroquinolyldipentamethylenediamine*, $C_9NH_{10} \cdot [CH_2]_5 \cdot C_9NH_{10}$, glistening crystals, m. p. 76°. The *picrate* softens at about 70°, and has m. p. below 90°.

Triethylamine and dibromopentane condense to a very hygroscopic compound, of which the *platinichloride* has m. p. 235°. Similar compounds are obtained from tripropyl-, tributyl-, and triamylamine.

1-Phenylpiperidine gives a pale red, hygroscopic compound; the *platinichloride*, $\{C_5NH_{10}Ph\}_2[CH_2]_5PtCl_6$, is a red, crystalline powder, m. p. 216°. Quinoline yields a yellowish-red, crystalline powder, $C_9NH_7Br \cdot [CH_2]_5 \cdot C_9NH_7Br$, m. p. 200°, with previous sintering. Tropine gives a white compound, $C_{21}H_{40}O_2N_2Br_2$, m. p. 282°, and strychnine a white compound, $C_{47}H_{83}O_6N_4Br_2$, which does not melt at 300°. J. C. C.

Stereoisomerism of Compounds Containing Asymmetric Carbon and Asymmetric Quinquevalent Nitrogen Atoms. MAX SCHOLTZ (*Ber.*, 1908, 41, 2005—2009).—The addition of an alkyl haloid to an active *N*-alkylated coniine, conhydrine (*Abstr.*, 1904, i, 1044; 1905, i, 296), or 2-phenyl-6-methylpiperidine (Scholtz and Wassermann, *Abstr.*, 1907, i, 340) results in the formation of two stereoisomeric quaternary ammonium compounds; active alkaloids, excepting the preceding, yield only one. Such isomerides have been obtained only from piperidine derivatives having a large substituent in position 2, and the theory is obvious that the existence of two stereoisomeric quaternary compounds is due to the influence of this substituent, which confers stability on the groups attached to the neighbouring nitrogen atom. To test the validity of the theory, α - and β -pipercolino have been converted into the *N*-ethyl derivatives, and, after resolution by tartaric acid, the *l*-forms of the tertiary base have been treated with benzyl bromide or iodide. In neither case have two isomerides been obtained. Moreover, the author showed some years ago (*Abstr.*, 1901, i, 749) that active amyl iodide and 1-methyl-2-pipercolino yield only one additive product. Hence it appears that a methyl group, whether directly attached to the asymmetric nitrogen

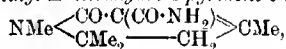
atom or in the α -position in the piperidine ring, cannot exert sufficient stabilising influence to ensure the formation of two stable stereo-isomeric quaternary compounds.

Hohenemser and Wolffenstein resolved 1-ethyl-2-pipecoline by means of the hydrogen tartrate, and found that the salt of the *d*-base separated first (Abstr., 1899, i, 936); the author, using the same method, obtained the salt of the *l*-base first. The discrepancy is attributed to the influence of temperature. 1-1-Benzyl-1-ethyl-2-pipecolinium iodide, m. p. 230°, has $[\alpha]_D -52.5^\circ$ in 10% alcoholic solution; the corresponding bromide, m. p. 237°, has $[\alpha]_D +20^\circ$ in the same solvent. The bromide of the inactive base has m. p. 204°.

1-Ethyl-3-pipecoline, b. p. 145.5–146.5°, was resolved by tartaric acid, and the active base so obtained had $D^{17} 0.8095$ and $[\alpha]_D -3.2^\circ$. 1-1-Benzyl-1-ethyl-3-pipecolinium iodide, m. p. 174°, crystallises in colourless needles. C. S.

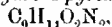
Hydrolysis of Oxyhydropyridine Nitriles. GALEAZZO PICCININI (*Atti R. Accad. Sci. Torino*, 1908, 43, 547–558. Compare this vol., i, 51).—The nitriles described in the former paper are not attacked by hydrochloric acid below 120°. The hydrolysis can be arrested before the elimination of the carboxyl group by employing 95–96% sulphuric acid at 150° as the hydrolysing agent. The amide is thus obtained, and may be converted into the acid by alkalis.

1:4:6:6-Tetramethyl- Δ^3 -tetrahydro-2-pyridone-3-carboxylamide,



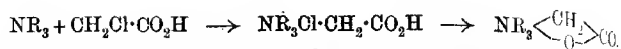
crystallises from alcohol in brilliant, colourless rosettes, or from water in large, monoclinic prisms, m. p. 195–196°. Its solution in water is neutral, but it dissolves readily in acids, and is precipitated by the usual reagents for alkaloids. Boiling with 50% sodium hydroxide solution is necessary to remove the NH_2 group. The corresponding carboxylic acid, $\text{C}_{10}\text{H}_{15}\text{O}_3\text{N}$, may be obtained by heating the nitrile with hydrochloric acid, $D 1.19$, for several hours at 120–125°, or by boiling the amide with 20% sulphuric acid, some decomposition of the acid occurring in the latter case, or best by the action of nitrous acid on the amide. It forms colourless prisms, m. p. 125–126° if rapidly, 118–120° (decomp.) if slowly, heated. The salts are readily soluble.

4:6:6-Trimethyl- Δ^3 -tetrahydro-2-pyridone-3-carboxylamide,

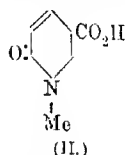
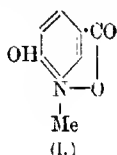


forms large, colourless prisms, m. p. 199–200° (corr.). Nitrous acid converts it into the carboxylic acid, $\text{C}_9\text{H}_{13}\text{O}_3\text{N}$, crystallising from water in long, colourless prisms, m. p. 116–117° (corr.). The sodium salt, $\text{C}_9\text{H}_{11}\text{O}_3\text{NNa} \cdot 2\text{H}_2\text{O}$, and the barium salt, $(\text{C}_9\text{H}_{12}\text{O}_3\text{N})_2\text{Ba} \cdot 3\text{H}_2\text{O}$, are described. C. H. B.

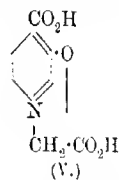
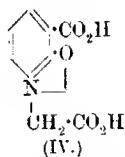
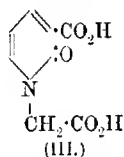
New Betaines of the Pyridine Series. ALFRED KIRPAL (*Monatsh.*, 1908, 29, 471–484).—According to Liebreich (*Ber.*, 1869, 2, 12), betaines are formed when tertiary bases are heated with chloroacetic acid and the products shaken with silver oxide:



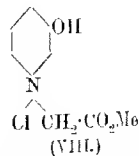
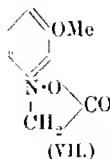
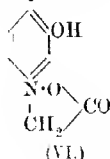
It is found now that, when heated with chloroacetic acid and treated with sulphuric acid, hydroxypyridinecarboxylic acids yield products which, according to the above scheme, should be the corresponding betaines, $\text{CO}_2\text{H}\cdot\text{C}_5\text{NH}_3(\text{OH})\text{C}(\text{CH}_2\text{CO}_2)\text{CO}_2\text{H}$. This structure, however, appeared doubtful, as on titration the products behaved as dibasic acids. Meyer has shown (Abstr., 1906, i, 108) that the action of methyl iodide on 6-hydroxynicotinic acid in alkaline solution leads to the formation, not of the expected betaine (I), but of the *N*-methyl derivative of the keto-acid (II).



In analogy to this, the product obtained from 2-hydroxynicotinic acid and chloroacetic acid might have the formula (III) or (IV), there being, similarly, two possibilities for the constitution of the product from 4-hydroxynicotinic acid, but that from 3-hydroxynicotinic acid, if not a betaine, can have only the formula (V).



It has been found, however, that 3-hydroxypyridinebetaine (VI) acts towards alkalis as a monobasic acid, and forms a silver salt, which with methyl iodide yields a methyl derivative; this does not react with ammonia, and must therefore be the ether (VII) (this vol., ii, 436). In agreement with this, it is found that the additive compound of 3-hydroxypyridine and methyl chloroacetate (VIII), on treatment with silver oxide, yields the betaine (VI), and not a chloride-free methyl ester.



The products obtained from the hydroxypyridinecarboxylic acids are therefore considered to be betaines, the second mol. of alkali being neutralised by the hydroxyl.

In connexion with the formation of methyl iodide when pyridine betaine is treated according to the Herzig-Meyer method (this vol., ii, 436), it is observed that von Gerichten found that pyridinebetaine hydrochloride, when heated at 200°, decomposes, forming pyridine, carbon dioxide, and methyl chloride (Abstr., 1882, 1109).

The *additive* compound of 3-hydroxypyridine and chloroacetic acid, $\text{OH}\cdot\text{C}_5\text{NH}_4\text{Cl}\cdot\text{CH}_2\cdot\text{CO}_2\cdot\text{C}_5\text{NH}_4(\text{OH})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, crystallises in colourless needles, m. p. 185° (decomp.). 3-Hydroxypyridinebetaine, $\text{C}_5\text{H}_5\text{O}_3\text{N}_2\text{H}_2\text{O}$, crystallises in colourless, rhombic plates, m. p. 182° (decomp.). The silver salt, $2\text{C}_5\text{H}_5\text{O}_3\text{NAg}\cdot 3\text{H}_2\text{O}$, was analysed. The methyl ester, $\text{C}_8\text{H}_9\text{O}_3\text{N}$, forms needles, m. p. 160° (decomp.).

The *additive* compound of 3-hydroxypyridine and methyl chloroacetate, $\text{C}_8\text{H}_{10}\text{O}_3\text{NCl}$, forms colourless plates, m. p. 155° (decomp.); the *platinichloride*, $(\text{C}_8\text{H}_9\text{O}_3\text{N})_2\cdot\text{H}_2\text{PtCl}_6\cdot 2\text{H}_2\text{O}$, crystallises in orange-yellow plates, m. p. 205°.

2-Hydroxynicotinic acid betaine (2-hydroxy-3-carboxypyridinebetaine), $\text{C}_8\text{H}_7\text{O}_5\text{N}$, crystallises in needles, m. p. 240°.

3-Hydroxy-4-carboxypyridinebetaine, prepared from 3-hydroxyisonicotinic acid, crystallises in needles, m. p. 200° (decomp.).

4-Hydroxy-3-carboxypyridinebetaine, prepared from 4-hydroxyisonicotinic acid, forms plates, m. p. 220° (decomp.). G. Y.

Quinoline-2-carboxyl Chloride. EMIL BESTHORN (*Ber.*, 1908, 41, 2003—2004).—The difference between Meyer (Abstr., 1905, i, 155, 666) and Besthorn and Ibele (Abstr., 1905, i, 612; 1906, i, 605) as to the physical properties of quinoline-2-carboxyl chloride is due to the fact that Kahlbaum's thionyl chloride contains a not inconsiderable amount of stannic chloride, which reacts with quinoline-2-carboxylic acid to form a substance insoluble in organic solvents. When thionyl chloride, free from tin, reacts with quinoline-2-carboxylic acid, the chloride, m. p. 97—98°, is obtained, the molecular weight of which, determined in benzene by the cryoscopic method, agrees with the formula $\text{C}_{10}\text{H}_6\text{ONCl}$. Meyer's chloride probably contained tin.

The presence of tin chloride in thionyl chloride is detected by the yellow colour produced by triphenylmethyl chloride, or by the splendid red coloration produced by *p*-tri-iodotriphenylmethyl chloride. A coloration is not produced in either case if pure thionyl chloride is used. C. S.

2-Quinolyl Phenyl Ketone. EMIL BESTHORN (*Ber.*, 1908, 41, 2001—2003).—The reaction between quinoline-2-carboxyl chloride and aluminium chloride in dry benzene leads to the formation of *2-quinolyl phenyl ketone*, $\text{C}_9\text{NH}_6\cdot\text{COPh}$, m. p. 110—111°, in good yield. The substance is colourless, and shows no tendency to yield dyes; consequently, it is doubtful whether the red substance, $\text{C}_{10}\text{H}_{12}\text{ON}_3$, obtained by Besthorn and Ibele (Abstr., 1904, i, 527) is 2:2'-di-quinolyl ketone. C. S.

Indolinones. D. LIEBER (*Monatsh.*, 1908, 29, 421—429).—Brunner has shown that the phenylhydrazides of fatty acids, or phenyl-substituted fatty acids, are converted into indolinones when heated with calcium oxide (Abstr., 1907, i, 240). This reaction has

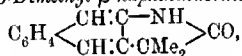
now been applied to the formation of indolinones from the α - and β -naphthylhydrazides of isobutyric acid.

isoButyryl- α -naphthylhydrazide, $C_{16}H_{17} \cdot NH \cdot NH \cdot C_4H_7O$, is obtained in a 86.3% yield by the action of isobutyric anhydride on α -naphthylhydrazine in benzene solution and extraction with water of the α -naphthylhydrazine isobutyrate, which is simultaneously formed. When heated with calcium oxide at 230° , it yields 3:3-dimethyl-

α -naphthindolinone, $\begin{array}{c} C_6H_4 - C - NH \\ | \quad | \\ CH:CH \cdot C \cdot CMe_2 \end{array} > CO$, which separates from dilute

alcohol in white crystals, m. p. 201° , and forms solutions with reddish-blue fluorescence. The methyl ether, $C_{16}H_{15}ON$, m. p. 78.5° , is formed by the action of sodium and methyl iodide on the indolinone in methyl-alcoholic solution. The acetyl derivative, $C_{16}H_{15}O_2N$, forms a crystalline mass, m. p. 106.5° . With mercuric chloride in concentrated alcoholic or aqueous solution, the indolinone yields a mixture of the mercurichloride and the free base; the salt is hydrolysed by excess of water.

isoButyryl- β -naphthylhydrazide is prepared in the same manner as the α -compound. 3:3-Dimethyl- β -naphthindolinone,



forms white crystals, m. p. 145.5° . The methyl ether, m. p. 155.5° .
The acetyl derivative, m. p. 139.5° . G. Y.

Tetrahydroacridine and a New Synthesis of Acridine. WILHELM BORSCHÉ [with H. TIEDTKE and W. ROTTSIEPER] (*Ber.*, 1908, 41, 2203—2208).—The hitherto unknown tetrahydrodibenzopyridines may be prepared by the following three methods: (1) Condensation of α -acyl cyclohexamethylene ketones with aniline and its homologues, and intramolecular condensation of the aniline-compounds initially formed. By this method, a mixture of the isomeric tetrahydroacridine and tetrahydrophenanthridine compound is obtained. (2) Condensation of aromatic *o*-amino-aldehydes or -ketones with hydroaromatic ketones containing a methylene group ortho to the carbonyl group. (3) The hydroaromatic ketone is treated with isatin and strong aqueous alkali, whereby tetrahydroacridine-5-carboxylic acid is formed. The latter, when heated, is converted into tetrahydroacridine with the evolution of carbon dioxide.

[With W. ROTTSIEPER].—*Tetrahydroacridine*, $C_{14}H_{14} \begin{array}{c} CH \\ \diagup \quad \diagdown \\ N \end{array} > C_6H_5$, is formed by heating *o*-aminobenzaldehyde with cyclohexanone at 130° , or by treating a solution of these substances in alcohol with a few drops of aqueous sodium hydroxide; it forms small, colourless plates, m. p. 51.5 — 55° . The picrate crystallises in small, yellow needles, m. p. 208 — 209° ; the methiodide, $C_{14}H_{16}NI$, is a yellow, crystalline powder, which sinters and then melts at 202 — 204° ; the platinumchloride, $(C_{14}H_{15}N)_2 \cdot H_2PtCl_6$, crystallises in small, brownish-yellow needles, m. p. 233 — 235° ; the aurichloride, $(C_{14}H_{15}N)_3 \cdot HCl \cdot 2HAnCl_4$, is a yellow, crystalline powder, m. p. 156 — 158° .

Tetrahydroacridine-5-carboxylic acid, $C_6H_4 \begin{smallmatrix} \swarrow C(CO_2H) \\ \searrow N \end{smallmatrix} C_6H_5$, crystallises in small, colourless leaflets, m. p. 284—286° (decomp.); the *hydrochloride*, $C_{14}H_{13}O_2N \cdot HCl$, crystallises in long, colourless needles, m. p. 233°. The *silver*, *lead*, and *calcium* salts are obtained as white precipitates from aqueous solutions of the *ammonium* salt; the *copper* salt is obtained as a green precipitate.

Acridine may be prepared from tetrahydroacridine or its carboxylic acid by distilling with litharge and passing the vapour over heated litharge (compare this vol., i, 365). W. H. G.

9:10-Phenanthraquinoline. FRIEDRICH HERSCHMANN (*Ber.*, 1908, 41, 1998—2000).—Skraup's synthesis has for the first time been applied in the phenanthrene series. The interaction of 9-amino-phenanthrene, nitrobenzene, glycerol, and concentrated sulphuric acid at 145—150° for four to five hours leads to the formation of a quinoline which must be 9:10-phenanthraquinoline, since ring-closure in the 9:8-positions would give a seven-membered ring. The compound forms long, colourless needles, and has m. p. 174°. The *nitrate*, m. p. 240°, *hydrochloride*, m. p. 248°, darkening at 245°, *sulphate*, *platinichloride*, and *picrate* are mentioned. The reaction with 2-amino-phenanthraquinone did not yield a pure product. C. S.

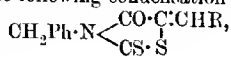
Substituted Rhodanic Acids and their Aldehyde Condensation Products. VII. RUDOLF ANDREASCH (*Monatsh.*, 1908, 29, 399—419. Compare *Abstr.*, 1907, i, 233).—The substituted rhodanic acids derived from *m*-toluidine, benzylamine, hydrazine, and glycine are now described in amplification of the previous papers on this subject.

3-*m*-Tolylrhodanic acid, $C_6H_4Me \cdot N \begin{smallmatrix} \swarrow CO \cdot CH_2 \\ \searrow CS \cdot S \end{smallmatrix}$, formed together with *ethyl m*-tolylldithiocarbaminacetate, $C_6H_4Me \cdot NH \cdot CS \cdot S \cdot CH_2 \cdot CO_2Et$, transparent prisms, m. p. 77°, from ammonium *m*-tolylldithiocarbamate and ethyl chloroacetate, crystallises in microscopic prisms, m. p. 148°.

The following *condensation products*, $C_6H_4Me \cdot N \begin{smallmatrix} \swarrow CO \cdot C \cdot CHR \\ \searrow CS \cdot S \end{smallmatrix}$, of 3-*m*-tolylrhodanic acid with aldehydes are described.

R=Ph: yellow needles, m. p. 124°; R= $C_6H_4 \cdot OH$ (o): yellow leaflets, becomes red at 190°, m. p. 220°; R= $C_6H_4 \cdot OAc$ (o): greyish-white scales, m. p. 231°; R= $C_6H_4 \cdot NO_2$ (m): chrome-yellow, microscopic needles, m. p. 234°; R= $C_6H_4 \cdot NMe_2$ (p): scarlet, crystalline powder, m. p. 140°, dyes wool, silk, and skin orange-yellow; R= $C_6H_4 \cdot O \cdot CH_2$: chrome-yellow, crystalline powder, m. p. 178°; R= CH_2CHPh : yellowish-brown powder, m. p. 145—146°.

3-Benzylrhodanic acid, $CH_2Ph \cdot N \begin{smallmatrix} \swarrow CO \cdot CH_2 \\ \searrow CS \cdot S \end{smallmatrix}$, prepared from benzylamine, carbon disulphide, and ethyl chloroacetate, crystallises in white leaflets, m. p. 83°. The following *condensation products*,

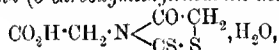


with aldehydes are described.

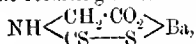
R = Ph: golden needles, m. p. 219°; R = $\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ (*m*): yellow needles, m. p. 183°, becomes superficially colourless on prolonged exposure to light; R = $\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$ (*p*): red needles with blue lustre, m. p. 177°.

The action of ethyl chloroacetate on hydrazine dithiocarbamate (Curtius and Heidenreich, Abstr., 1894, i, 166) leads to the formation of 3-aminorhodanic acid, $\text{NH}\cdot\text{N}\begin{smallmatrix} \text{CO}\cdot\text{CH}_2 \\ \text{CS}\cdot\text{S} \end{smallmatrix}$, which crystallises in slightly yellow needles, m. p. 92°, together with a crystalline substance, $\text{C}_{10}\text{H}_{14}\text{O}_4\text{N}_2\text{S}_2$, m. p. 60°. 3-Aminorhodanic acid forms condensation products with *m*-nitrobenzaldehyde, $\text{NH}_2\cdot\text{N}\begin{smallmatrix} \text{CO}\cdot\text{C}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2 \\ \text{CS}\cdot\text{S} \end{smallmatrix}$, yellow needles, m. p. 175–176°, and *p*-dimethylaminobenzaldehyde, $\text{C}_2\text{H}_5\text{ON}\text{S}_2\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$, red, microscopic plates, commences to decompose at 200°, m. p. 266°.

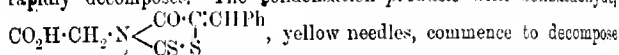
Rhodaninacetic acid (3-carboxymethylrhodanic acid),



is formed as the barium salt by the action of carbon disulphide and baryta on glycine (compare Siegfried, Abstr., 1905, ii, 332; 1906, i, 324) and treatment of the resulting barium dithiocarbamate,



with ethyl chloroacetate. The rhodaninacetic acid crystallises in needles or leaflets, loses H_2O at 100°, or partially in a vacuum, m. p. 145°, and forms a white lead and green copper salt; the red silver salt rapidly decomposes. The condensation products with benzaldehyde,



at 200°, m. p. 240°; *m*-nitrobenzaldehyde, $\text{C}_{13}\text{H}_9\text{O}_3\text{N}_3\text{S}_2$, yellow needles, commences to decompose at 200°, m. p. 270–280°, and *p*-dimethylaminobenzaldehyde, $\text{C}_{14}\text{H}_{14}\text{O}_3\text{N}_2\text{S}_2$, orange-red plates, m. p. 235° (decomp.), are described.

Rhodanic acids are obtained also from other amino-acids, such as alanine and aminobenzoic acid; that from asparagine yields a crystalline benzylidene derivative. Analogous substances are formed from the hydrolysis products of gelatin and from Witte's peptone. G. Y.

Action of Formaldehyde on Secondary Aromatic Amines. JULIUS VON BRAUN (*Ber.*, 1908, 41, 2145–2156).—When formaldehyde acts on methylaniline or its aliphatic homologues in neutral or alkaline solution, condensation readily occurs with production of derivatives of methylenediamine. In the case of methyl-*o*-toluidine, however, the reaction is more sluggish, and still more so with methyl-*p*-toluidine. On boiling diphenyl-, dimethyl-, or diethyl-methylenediamine with acids or by treating methyl- or ethylaniline (2 mols.) with formaldehyde (1 mol.) in acid solution, the product is in each case the same; it consists of a mixture of the original secondary base, the diphenylmethane derivative, and a more complex substance containing about $1\frac{1}{2}$ mols. of the formaldehyde residue to 2 mols. of the base.

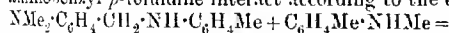
The latter is formed in larger amount when a greater excess of formaldehyde is employed; it is formed probably from a further condensation of formaldehyde with the diphenylmethane base, involving the elimination of the hydrogen atom in the ortho-position to the nitrogen and the condensation of a further amount of methylaniline. This explanation is confirmed by the fact that methyl-*o*- and -*p*-toluidines furnish only very small amounts of these complex substances, the diphenylmethane bases derived from them containing only half as many *o*-hydrogen atoms as in the case of that derived from methylaniline.

s-Diphenyldimethylmethylenediamine, $\text{CH}_2(\text{NPhMe})_2$, prepared from methylaniline and formaldehyde in presence of alkali, forms a mass of white crystals, m. p. 35°. *s*-Diphenyldiethylmethylenediamine, $\text{CH}_2(\text{NPhEt})_2$,

forms white, glistening needles, m. p. 79°, b. p. 205°/9 mm. Diethyldiaminodiphenylmethane, $\text{CH}_2(\text{C}_6\text{H}_4\cdot\text{NHEt})_2$, prepared from formaldehyde and ethylaniline in presence of hydrochloric acid, is a pale yellow liquid, b. p. 255°/10 mm.; the nitroso-derivative has m. p. 83°, and the phenylthiocarbamide, white leaflets, has m. p. 153°. For investigating the action of formaldehyde on methyl-*o*-toluidine, the latter was prepared by the action of cyanogen bromide on dimethyl-*o*-toluidine in the same way as described for methyl-*p*-toluidine (this vol., i, 626). The *o*-tolylmethylcyanamide produced in the reaction has b. p. 135—136°/8 mm., and, on boiling with 30% sulphuric acid for twenty hours, yields methyl-*o*-toluidine and a small amount of dimethyldiaminodi-*o*-tolylmethane. *o*-Tolylecyanamide in contrast to this furnishes *o*-toluidine and *o*-tolylcarbamide.

s-Di-*o*-tolyl dimethylmethylenediamine, $\text{CH}_2(\text{NMe}\cdot\text{C}_6\text{H}_4\cdot\text{Me})_2$, has b. p. 212—215°/18 mm.; it yields dimethyldiaminodi-*o*-tolylmethane when boiled with acids. *s*-Di-*p*-tolyl dimethylmethylenediamine forms white crystals, m. p. 68°. Dimethyldiaminodi-*p*-tolylmethane is a tough, gummy substance; the nitroso-derivative is a yellow, crystalline powder, m. p. 123°.

The difference exhibited by methylaniline and methyl-*o*-toluidine in their behaviour towards formaldehyde is also shown in the conversion of aminobenzyl bases into diphenylmethane bases by boiling with amines in acid solution. Thus, whilst methyl-*o*-toluidine and dimethylaminobenzyl-*p*-toluidine interact according to the equation



$\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{Me}\cdot\text{NHMe} + \text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{Me}$, methylaniline furnishes a complex substance similar to that obtained in the formaldehyde condensation, together with *p*-toluidine and trimethyldiaminodiphenylmethane, $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHMe}$, b. p. 245—246°/9 mm., m. p. 57°, the nitroso-derivative of which forms small, yellow crystals, m. p. 96—97°. J. C. C.

Synthesis of *s*-Diphenylcadaverine. [*s*-Diphenylpentamethylenediamine]. JULIUS VON BRAUN (*Ber.*, 1908, 41, 2165—2168).—*s*-Diphenylpentamethylenediamine has been prepared in two ways, namely, (1) aniline is converted by means of α -dibromo-*n*-pentane into 1 phenylpiperidine, this with cyanogen bromide gives

phenyl- ω -bromoamylcyanamide (Abstr., 1907, i, 960), which is condensed with aniline, forming cyanodiphenylpentamethylenediamine, this being hydrolysed finally. (2) Methylaniline is converted into *s*-diphenyldimethylpentamethylenediamine (this vol., i, 678), which is treated with cyanogen bromide, and the resulting *s*-dicyanodiphenylpentamethylenediamine is hydrolysed.

Cyanodiphenylpentamethylenediamine, $\text{CN}\cdot\text{NPh}\cdot[\text{CH}_2]_5\cdot\text{NPh}\cdot\text{CN}$, forms small, colourless crystals, m. p. 67° ; the *hydrochloride* has m. p. 101° . *Dicyanodiphenylpentamethylenediamine*,

$\text{CN}\cdot\text{NPh}\cdot[\text{CH}_2]_5\cdot\text{NPh}\cdot\text{CN}$, forms white, bushy needles, m. p. 76° . *s*-Diphenylpentamethylenediamine, $\text{NPh}\cdot[\text{CH}_2]_5\cdot\text{NPh}$, has m. p. 45° , b. p. $260-265^\circ/10\text{ mm.}$; the *hydrochloride*, m. p. $193-194^\circ$, the *dibenzoyl* derivative,

$\text{NPhBz}\cdot[\text{CH}_2]_5\cdot\text{NPhBz}$, hard, glistening crystals, m. p. 124° , and the *dinitroso*-derivative, $\text{NO}\cdot\text{NPh}\cdot[\text{CH}_2]_5\cdot\text{NPh}\cdot\text{NO}$, m. p. 60° , are described. J. C. C.

Coloured Salts of Schiff's Bases. II. Hydrochlorides of Bases formed by Condensing Phenyl-*p*-phenylenediamine with Aromatic Aldehydes. FORRIS J. MOORE and R. (t. WOODBRIDGE, *J. Amer. Chem. Soc.*, 1908, 30, 1001-1004).—Moore and Gale (this vol., i, 368) have shown that the bases obtained by condensing *p*-phenylenediamine with aromatic aldehydes unite with hydrogen chloride in two proportions, forming dark red hydrochlorides and yellow dihydrochlorides.

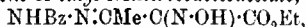
It is now found that phenyl-*p*-phenylenediamine behaves in a similar manner, but that the dihydrochlorides are formed less readily. All the dihydrochlorides, however, with the exception of that of phenylcinnamylidene-*p*-phenylenediamine, are so stable as to retain their 2 mols. of hydrogen chloride when dried over sodium hydroxide in a vacuum desiccator. The dihydrochloride of the cinnamylidene compound, under these conditions, gradually darkens and loses 1 mol. of hydrogen chloride.

The *mono*- and *di*-hydrochlorides of the following bases have been prepared: benzylidene- and salicylidene-phenyl-*p*-phenylenediamines (Hefcke, Abstr., 1889, 609); phenylpiperonylidene-*p*-phenylenediamine, m. p. 116° ; phenylanisylidene-*p*-phenylenediamine, m. p. 103° , which forms silver-grey, pearly scales, and phenylcinnamylidene-*p*-phenylenediamine, m. p. 145° , which crystallises in brilliant yellow scales. E. G.

Isomeric Modifications of *p*-Tolildioxime and their Behaviour as to Formation of Complexes. LEO A. TSCHEGGEFF and L. SEIKO (*Ber.*, 1908, 41, 2219-2231).—The conclusion previously drawn that only the *syn*-forms of 1:2-dioximes give complex metallic compounds with nickel, cobalt, or ferrous salts (this vol., i, 554) is further supported by the behaviour of the *p*-tolildioximes; the *amphi*- and *anti*-compounds give negative results, whereas the *syn*-modifications give with nickel salts a red precipitate, with ammonium palladium chloride and pyridine an orange-red precipitate, and with ferrous sulphate and pyridine a reddish-violet coloration.

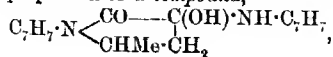
The *syn*- and *anti*-*p*-tolildioximes have already been prepared by Stierlin (Abstr., 1889, 513); the *amphi*-compound was obtained as follows: On oxidising *p*-tolualdoxime by Beckmann's method (Abstr., 1899, 980), *p*-tolualdoxime peroxide, $(C_6H_4Me \cdot CH:N)_2O_2$, is obtained as glistening needles, m. p. 108° . It is insoluble in alkali, and is reduced by ammonium sulphide to aldoxime. By passing nitrous fumes into an ethereal suspension of the peroxide, or, better, into a solution of the aldoxime until almost complete solution of the crystals has occurred, *p*-tolildioxime peroxide, $C_{16}H_{11}O_2N_2$, is obtained, separating from light petroloum in crystals, m. p. 142° . *amphi-p*-Tolildioxime, $C_{16}H_{16}O_2N_2$, obtained by reducing the peroxide in alcoholic solution with zinc dust and acetic acid, forms white needles, which contain 1 mol. of chloroform of crystallisation when this solvent is used. The chloroform-free substance melts on placing it in a bath at 200° , immediately resolidifies, and then has m. p. 229 — 230° , a phenomenon also characteristic of γ -benzildioxime. It is readily converted into the β -modification at 200° . W. R.

The Benzoylhydrazone of Ethyl *iso*Nitrosoacetoacetate and its Fission Products. CARL BÜLOW and FRITZ SCHAUB (*Ber.*, 1908, 41, 2181—2183).—When the benzoylhydrazone of ethyl *isonitroso*-acetoacetate is evaporated with aqueous ammonia or allowed to remain with concentrated sulphuric acid for eight hours, or boiled with alcohol for seventy-one hours, it is decomposed into ethyl alcohol, benzoic acid, and 4-*isonitroso*-3-methylpyrazolone (compare Knorr, Abstr., 1903, i, 660; Betti, Abstr., 1904, i, 533; Wolff, *ibid.*, 722). The benzoylhydrazone of ethyl *isonitroso*acetoacetate,

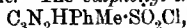


sinters at 164.5° , and is completely decomposed at 173° . The properties of 4-*isonitroso*-3-methylpyrazolone are correctly given by Betti, and the m. p. is 230 — 231° (Betti gives 230°). J. C. C.

The Mechanism of the Synthesis of Cyclic Nitrogen Compounds [Quinoline Derivatives]. LOUIS J. SIMON (*Compt. rend.*, 1908, 146, 1400—1402).—In view of the results obtained in the condensation of ethyl oxalacetate with primary amines (Simon and Conduché, Abstr., 1907, i, 963; Simon and Mauguin, this vol., i, 296), the author has repeated his work on the action of pyruvic acid on *p*-toluidine (Abstr., 1898, i, 152) when molecular proportions are mixed in chloroform solution in the cold. The chief product is a very unstable compound, which is readily changed by the action of solvents or heat, or even after some time. This is not *p*-tolilpyruvic acid (*loc. cit.*), but a more complex substance, probably of the constitution $CO_2H \cdot CMe(NH \cdot C_6H_7) \cdot CH_2 \cdot C(OH)(NH \cdot C_6H_7) \cdot CO_2H$, which when treated with boiling water yields *p*-toluidine and 2:6-dimethylquinoline-4-carboxylic acid, decomposing at 265° and furnishing 2:6-dimethylquinoline. The ethyl ester has m. p. 74° . In the same reaction is also produced a small proportion of a compound,

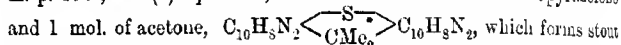


when heated with concentrated hydrochloric acid at 150° is decomposed, forming sulphuric acid and 1-phenyl-3-methylpyrazole. The sodium, $C_{10}H_8N_2 \cdot SO_3Na$, and barium, $(+H_2O)$, salts were analysed. On treatment with bromine water, the sulphonic acid yields 4-bromo-1-phenyl-3-methylpyrazole-5-sulphonic acid, m. p. 225° , which yields sulphuric acid and 4-bromo-1-phenyl-3-methylpyrazole when heated with an excess of bromine. The sulphonyl chloride,

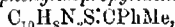


formed by heating the sulphonic acid with phosphorus pentachloride, crystallises in white needles, m. p. 101° , and is hydrolysed by hot water, forming the acid. The sulphonamide, $C_{10}H_8N_2 \cdot SO_2 \cdot NH_2$, prepared by shaking the sulphonyl chloride with ammonium carbonate, crystallises in white prisms, m. p. 243° , and is soluble in aqueous sodium hydroxide. The anilide, $C_{10}H_8N_2 \cdot SO_2 \cdot NHPh$, crystallises in needles, m. p. 127° .

The thiopyrazolone reacts with benzaldehyde when heated, forming the 4-benzylidene derivative, $C_{10}H_8N_2S \cdot CHPh$, which crystallises in white needles, m. p. $183-184^\circ$. On prolonged heating, the thiopyrazolone and benzaldehyde yield an amorphous product, m. p. 191° . The action of acetone on thiopyrazolone leads to the formation of (a) the 4-isopropylidene derivative, $C_{10}H_8N_2S \cdot CMe_2$, which crystallises in needles, m. p. 204° , is sparingly soluble in alcohol, and when treated with permanganate in acetic acid solution yields a crystalline substance, m. p. 150° , and (b) a product, formed from 2 mols. of the thiopyrazolone

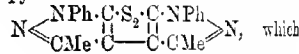


which forms stout crystals, m. p. 176° , and is more soluble in alcohol and ether than the preceding condensation product. With acetophenone, the thiopyrazolone forms a 4-phenylisopropylidene derivative,



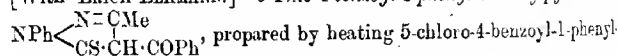
crystallising in yellow needles, m. p. $135-136^\circ$.

When heated with alkalis or concentrated acids, 4-bromo-5-benzoylthio-1-phenyl-3-methyl-4:5-dihydropyrazole is converted into bis-5-thio-1-phenyl-3-methylpyrazolone,

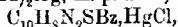


which crystallises in white needles, m. p. 198° , is stable towards oxidising and reducing agents, and forms a methiodide, $C_{20}H_{16}N_4S_2MeI$, crystallising in white needles, m. p. 198° , losing methyl iodide.

5-Thio-4-benzoyl-1-phenyl-3-methylpyrazolone and its Derivatives.—[With ERICH LEHMANN.]—5-Thio-4-benzoyl-1-phenyl-3-methylpyrazolone



prepared by heating 5-chloro-4-benzoyl-1-phenyl-3-methylpyrazole with sodium hydrogen sulphide in alcoholic solution crystallises in dark yellow needles with red lustre, m. p. 112° , and forms an unstable hydrochloride, crystallising in needles. The mercuric salt, $(C_{10}H_8N_2SBz)_2Hg$, m. p. 291° , and the mercurichloride,

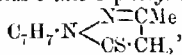


white needles, m. p. 223° , were analysed. If the 5-chloropyrazole is heated with alcoholic sodium hydrogen sulphide in a sealed tube at 150° , it forms a substance, m. p. 174° . When oxidised with hydrogen

peroxide in alkaline solution, the thiopyrazolone yields 4-benzoyl-1-phenyl-3-methylpyrazole-5-sulphonic acid, which is amorphous, and is hydrolysed by concentrated hydrochloric acid, forming hydrochloric acid and 1-phenyl-4-benzoyl-3-methylpyrazole. One oxidation of the thiopyrazolone with hydrogen peroxide led to the formation of a crystalline substance, m. p. 84°. Oxidation of the thiopyrazolone with iodine in alkaline solution leads to the formation of the disulphide, $(C_{10}H_8N_2Bz)_2S_2$, which is obtained as a by-product in the preparation of the thiopyrazolone from the 5-chloropyrazole; it crystallises in yellow plates, m. p. 156°, and dissolves in concentrated hydrochloric acid.

5-Methylthiol-4-benzoyl-1-phenyl-3-methylpyrazole (4-benzoyl-ψ-thiopyrine), $COPh \cdot C_3N_2PhMe \cdot SMe$, formed by the action of methyl iodide on the thiopyrazolone in alkaline solution, crystallises in white needles, m. p. 78°, and on oxidation with permanganate in glacial acetic solution yields the sulphone, $COPh \cdot C_3N_2PhMe \cdot SO_2Me$, crystallising in colourless plates, m. p. 167°. The 5-ethylthiol compound, $COPh \cdot C_3N_2PhMe \cdot SEt$, colourless plates, m. p. 98°, is formed by the action of ethyl iodide on the thiopyrazolone in alkaline solution, or by the action of mercaptan and sodium ethoxide on the 5-chloropyrazole. The ethylsulphone, $C_{13}H_{18}O_3N_2S$, crystallises in colourless needles, m. p. 122°. The 5-phenylthiol compound, $COPh \cdot C_3N_2PhMe \cdot SPh$, cannot be prepared from the thiopyrazolone, but is obtained by heating the 5-chloropyrazole with thiophenol and sodium ethoxide; it crystallises in colourless needles, m. p. 104°, and yields sulphuric acid when heated with nitric acid only at 300°. The sulphone, $C_{23}H_{18}O_3N_2S$, forms colourless needles, m. p. 125°, and when heated with phenylhydrazine is reduced to the phenylthiol compound. The benzyl ether, $COPh \cdot C_3N_2PhMe \cdot S \cdot CH_2Ph$, is formed from benzyl chloride and the thiopyrazolone; it crystallises in needles, m. p. 116°. The 5-benzoyl derivative, $C_{10}H_8N_2SBz$, prepared by shaking the thiopyrazolone with benzoyl chloride in alkaline solution, crystallises in needles, m. p. 107°. The carboxymethyl ether, $COPh \cdot C_3N_2PhMe \cdot S \cdot CH_2 \cdot CO_2H$, formed from the thiopyrazolone and chloroacetic acid, is obtained in colourless crystals, m. p. 124°, and is soluble in dilute alkalis.

5-Thio-1-p-tolyl-3-methylpyrazolones and its Derivatives. — [With ERICH DULK.]—p-Tolylthiopyrine, m. p. 212°, which will be described later, is converted into 5-benzoylthio-1-p-tolyl-3-methylpyrazolone, b. p. 190–200°/15 mm., in the same manner as that employed with the phenyl compound. On hydrolysis with alcoholic potassium hydroxide, the benzoyl compound yields 5-thio-1-p-tolyl-3-methylpyrazolone,



which is also formed from 1-p-tolyl-3-methylpyrazolone by Stoermer and Johannsen's method (Abstr., 1907, i, 966); it is obtained in large, rhombic crystals, m. p. 135°, and behaves towards alkalis and acids in the same manner as the phenyl compound. The hydrochloride,



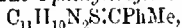
colourless plates; the mercuric salt, $(C_{11}H_{11}N_2S)_2Hg$, needles, m. p. 142°; the mercurichloride, $C_{11}H_{11}N_2S \cdot HgCl$, prisms, m. p. 208°. The methiodide, $C_{11}H_{12}N_2S \cdot MeI$, formed by the action of methyl iodide on

the thiopyrazole, has m. p. 175°, and is converted by water into the liquid methyl ether. The benzoyl derivative, $C_{11}H_{11}N_2 \cdot SBz$, crystallises in white needles, m. p. 114°, and forms a 4-bromo derivative, $C_{11}H_{10}N_2Br \cdot SBz$, which crystallises in prisms, m. p. 104°, yields benzoic acid and hydrogen bromide when heated with concentrated hydrochloric acid, and appears to form 4-bromo-1-p-tolyl-3-methylpyrazolone when treated with alkalis. The disulphide, $S_2(C_{11}H_{11}N_2)_2$, forms a yellowish-green mass, m. p. 74°, and is soluble in concentrated hydrochloric acid, being reprecipitated unchanged by water. The 5-sulphonic acid, $C_{11}H_{11}N_2 \cdot SO_3H$, crystallises in white prisms, m. p. 246°; the barium salt, $(C_{11}H_{10}O_3N_2S)_2Ba$, forms small prisms. The sulphonyl chloride, $C_{11}H_{11}N_2 \cdot SO_2Cl$, white needles, m. p. 77°. The sulphonamide, $C_{11}H_{11}N_2 \cdot SO_2 \cdot NH_2$, prisms, m. p. 227°. The sulphonanilide, $C_{11}H_{11}N_2 \cdot SO_2 \cdot NHPh$, needles, m. p. 118°.

The 4-benzylidene derivative, $C_{11}H_{10}N_2S \cdot CHPh$, crystallises in white needles, m. p. 212°. When heated with the calculated amount of acetone, the thiopyrazolone yields the 4-isopropylidene compound,



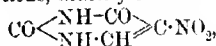
crystallising in colourless needles, m. p. 206°, but if with an excess of acetone and alcohol or a large excess of acetone alone, it forms the condensation product, $C_{11}H_{10}N_2 \cdot \begin{smallmatrix} S \\ \diagup \quad \diagdown \\ CMe_2 \end{smallmatrix} C_{11}H_{10}N_2$, which crystallises in needles, m. p. 186°. The 4-phenylethylidene derivative,



formed from the thiopyrazolone and acetophenone, crystallises in colourless needles, m. p. 106°. G. Y.

Pyrimidines. VIII. Separation of Thymine from Uracil. TREAT B. JOHNSON (*J. Biol. Chem.*, 1908, 4, 407—418).—When thymine is dissolved in cold fuming nitric acid (D 1.5) and evaporated, crystals of nitrohydroxyhydrothymine, $CO \cdot \begin{smallmatrix} NH \\ \diagup \quad \diagdown \\ NH \cdot CH(OH) \end{smallmatrix} \cdot CO \cdot CMe \cdot NO_2$, are formed, which generally melt with effervescence at 183—185° (α-variety), but sometimes at 230—235° (efferv.); on keeping, the latter modification is spontaneously transformed into the former. Both modifications when reduced yield the original thymine.

Under the same conditions, uracil yields 5-nitrouracil,

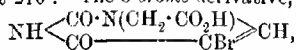


which requires 800 to 900 parts of cold alcohol for complete solution, and can be reduced to amino-uracil. Since nitrohydroxyhydrothymine is very soluble in cold alcohol, a separation of the two substances can be readily effected by nitration. One gram of the mixture is dissolved in 10 c.c. of nitric acid (D 1.5); after evaporation of the solution below 60°, the residue is extracted with 15 c.c. of cold alcohol. The nitro-compounds can be purified by crystallisation from hot water and alcohol. C. B.

Pyrimidines. XXXI. Synthesis of Uracil-3-acetic Acid. HENRY L. WHEELER and LEONARD M. LIDDLE (*J. Amer. Chem. Soc.*, 1908, 30, 1152—1156).—Johnson and Heyl (*Abstr.*, 1907, i, 728) have

found that when 2-ethylthiol-6-pyrimidone is treated with methyl iodide in presence of potassium hydroxide, 2-ethylthiol-1-methyl-6-pyrimidone is produced. When, however, 2-ethylthiol-6-pyrimidone is treated with ethyl chloroacetate and alkali hydroxide, alkylation takes place in the 3 position with formation of *ethyl 2-ethylthiol-6-pyrimidone-3-acetate*, $\text{N} \begin{smallmatrix} \text{C}(\text{SEt}) \cdot \text{N}(\text{CH}_2 \cdot \text{CO}_2\text{Et}) \\ \text{CO} \end{smallmatrix} \text{CH} \text{CH}$, m. p. 129°, which crystallises in long, colourless prisms. The corresponding *acid*, m. p. 208—209°, forms slender prisms, and can be prepared either by the hydrolysis of the ester or by heating 2-ethylthiol-6-pyrimidone with potassium chloroacetate. When the acid is warmed with hydrochloric acid, mercaptan is evolved and uracil-3-acetic acid is produced.

Uracil-3-acetic acid, $\text{NH} \begin{smallmatrix} \text{CO} \cdot \text{N}(\text{CH}_2 \cdot \text{CO}_2\text{H}) \\ \text{CO} \end{smallmatrix} \text{CH} \text{CH}$, m. p. 235° (decomp.), prepared by heating an alkaline solution of uracil with chloroacetic acid, forms small tablets; its *potassium*, *copper*, and *barium* salts are described. The *methyl* ester melts partly at about 177°, and completely at about 216°. The 5-bromo-derivative,



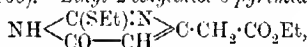
m. p. 241° (decomp.), forms colourless needles. The corresponding 5-nitro-derivative, m. p. 264—265° (decomp.), crystallises in colourless prisms.

1-Methyluracil-3-acetic acid, $\text{NMe} \begin{smallmatrix} \text{CO} \cdot \text{N}(\text{CH}_2 \cdot \text{CO}_2\text{H}) \\ \text{CO} \end{smallmatrix} \text{CH} \text{CH}$, m. p. 239—240°, prepared by the action of potassium chloroacetate on methyluracil or by treating uracil-3-acetic acid with methyl iodide in presence of potassium hydroxide, crystallises in needles or prisms.

E. G.

Pyrimidines. XXXII. Synthesis of Uracil-4-acetic Acid.

HENRY L. WHEELER and LEONARD M. LIDDLE (*J. Amer. Chem. Soc.*, 1968, 80, 1156—1160).—*Ethyl 2-ethylthiol-6-pyrimidone-4-acetate*,

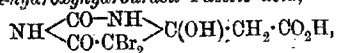


m. p. 131°, prepared by the action of ethyl acetonedicarboxylate on an alkaline solution of the ethyl bromide additive product of thiocarbamide, forms long, colourless, silky needles. The corresponding *acid*, m. p. 155° (decomp.), crystallises in colourless needles, and when heated at 170° is converted into 2-ethylthiol-4-methyl-6-pyrimidone. When this acid is warmed with strong hydrochloric acid, mercaptan is evolved and uracil-4-acetic acid is produced.

Uracil-4-acetic acid, $\text{NH} \begin{smallmatrix} \text{CO} \cdot \text{NH}_2 \\ \text{CO} \end{smallmatrix} \text{CH} \text{CH} \text{C} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, m. p. 340° (decomp.), crystallises in flat prisms and is soluble in about 8 parts of boiling water and in 30 parts of cold water; its *potassium* salt is described. The *ethyl* ester, m. p. 187—189°, crystallises with H_2O . The *methyl* ester has m. p. 216—218°. *5-Nitro-uracil-4-acetic acid*, m. p. 153° (decomp.), forms minute cubes.

By the action of bromine on an aqueous solution of uracil-4-acetic

acid, 5-dibromo-4-hydroxyhydrouacil-4-acetic acid,



m. p. 240° (decomp.), is produced, which forms colourless plates, probably containing $\frac{1}{2}\text{H}_2\text{O}$.

E. G.

α -Chloro- β -iminazolypropionic Acid. ADOLF WINDAUS and W. VOET (*Beitr. chem. Physiol. Path.*, 1908, 11, 406—408).—By employing the method already given by Fränkel (*Abstr.*, 1906, i, 547) for preparing chlorohistidinecarboxylic acid by treating histidine hydrochloride with nitrous acid and subsequent treatment of the crude product so obtained with zinc dust and glacial acetic acid, the authors have succeeded in obtaining only β -iminazolypropionic acid. The chlorohistidinecarboxylic acid was, however, obtained by the following method. Histidine was treated with hot potassium nitrate in concentrated hydrochloric acid; the crude hydrochloride of chlorohistidinecarboxylic acid was then esterified by 10% alcoholic hydrogen chloride, and the hydrochloride of the ester thus obtained was precipitated from alcoholic solution by means of ether. This was converted into the oxalate, m. p. 161°. The free ester is an oil, from which, by saponification, pure chlorohistidinecarboxylic acid can be obtained. This melts at 191° (decomp.).

β -Iminazolypropionic acid, on the other hand, which agrees in properties with the substance described by Fränkel as chlorohistidinecarboxylic acid, has m. p. 80°, and when heated loses H_2O .

S. B. S.

Hydroxyquinoxalines. OTTO HINSBERG (*Ber.*, 1908, 41, 2031—2033).—Five compounds, $\text{C}_8\text{H}_6\text{O}_2\text{N}_2$, have been prepared; these have been termed: 1. Dihydroxyquinoxaline (Bladin, *Abstr.*, 1885, 785); 2. Dihydroxyethylenephenylenediamine (Aschan, *ibid.*, 1886, 147); 3. Dihydroxyquinoxalino (Hinsberg and Pollak, *ibid.*, 1896, i, 394); 4. Phenyleneoxamide (Seeliger and Meyer, *ibid.*, 1897, i, 45); 5. Phenyleneoxamide (Motylowski, this vol., i, 371). Compounds 2 to 5 are shown to be identical. Although compounds 1 and 3 were previously stated to be identical, it is now shown that they are different substances. Hinsberg and Pollak's compound, unlike Bladin's, does not combine with water of crystallisation.

Motylowski's oxidation product of hydroxydihydroquinoxaline is probably identical with 2-hydroxyquinoxaline.

J. J. S.

Synthesis of Phenylquinoxalines. OTTO FISCHER and FEIZ RÖMER (*Ber.*, 1908, 41, 2350—2353).—Fischer and Schindler described recently (this vol., i, 221) the formation of 2- and 3-phenylnaphthaquinoxalines from diketo- $\alpha\beta$ -naphthazine and diketo- $\alpha\alpha\beta$ -naphthazine respectively. As the *o*-phenylnaphthaquinoxalines were previously unknown, and in their properties differed markedly from Feist and Arnstein's phenylnaphthaquinoxaline prepared from β -naphthaquinone and phenylethylenediamine (*Abstr.*, 1895, i, 258), it was advisable to confirm their constitution by synthesis. For this purpose, the authors employed Hinsberg's method for the preparation of phenylquinoxalines from bromoacetophenone and *o*-diamines, and

found that the action of bromoacetophenone on 1:2-diaminonaphthalene leads to the formation of the two products described by Fischer and Schindler, but in small yields and accompanied by much resin. Better yields are obtained by employing isonitrosoacetophenone, which reacts more smoothly than does bromoacetophenone with *o*-diamines, and with *o*-phenylenediamine gives good yields of phenylquinoxaline (Hinsberg, Abstr., 1897, i, 120).

Fischer and Schindler's phenylnaphthaquinoxalines are formed when isonitrosoacetophenone and 1:2-diaminonaphthalene are boiled in molecular proportions in methyl-alcoholic solution. The 2-phenyl-compound is now found to be white. Both quinoxalines are volatile with steam, and give with zinc dust and acetic acid a transient red coloration. If boiled in ethyl-alcoholic solution, isonitrosoacetophenone and 1:2-diaminonaphthalene form, together with the quinoxalines, a substance, which separates from pyridine in red crystals, and gives green and blue colorations with concentrated sulphuric acid. This red substance is not formed in presence of small amounts of hydroxylamine hydrochloride.

The repetition of Feist and Arnstein's experiment shows that these authors could not have obtained a single substance. The action of ethylenediamine, which oxidises more easily than phenylethylenediamine, on β -naphthaquinone leads to the formation of naphthaquinoxaline (Hinsberg, Abstr., 1890, 972). The *picrate*, $C_{13}H_{11}O_7N_5$, crystallises in yellow needles, m. p. 171°. G. Y.

Preparation of Isatin and its Methyl Derivative. RUDOLPH BAUER (D.R.-P. 193633).—It has been found that isatin and its methyl derivatives can be produced by the action of warm concentrated sulphuric acid on substituted iminochlorides having the general formula $RN:CCI:CCI:NR$, where R is a phenyl or tolyl group. Diphenyloxaliminochloride, m. p. 115°, di-*o*-tolylloxaliminochloride, m. p. 131°, di-*m*-tolylloxaliminochloride, yellow prisms, m. p. 72°, and di-*p*-tolylloxaliminochloride, yellow leaflets, m. p. 107°, were employed in this synthesis. *o*-Methylisatin, which is fully described for the first time, yields a *phenylhydrazone*, golden needles, m. p. 242°, and *oxime*, yellow needles, m. p. 235°. G. T. M.

Preparation of Stable Chloroindigotins. GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 193971).—A stable chloroindigotin, $C_{16}H_6O_5N_2Cl$, is obtained by passing chlorine into a mixture of finely powdered indigotin and nitrobenzene. A vigorous reaction occurs, and the chloro-derivative is produced in a crystalline form. When reduced with alkaline hyposulphite, this substance furnishes a light yellow leuco-derivative, which has valuable tinctorial properties. G. T. M.

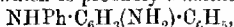
Preparation of Halogen Derivatives of β -Naphthindigotin. GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 193970).—*Bromo- β -naphthindigotin* is prepared by successively brominating β -naphthisatin, converting the bromo-derivative into the chloride, reducing the latter with hydriodic acid or some other suitable reducing agent, and finally oxidising the product with air in the presence of sodium hydroxide. The product is a dark green, crystalline

powder, which furnishes a reddish-brown leuco-derivative giving fast shades of blue on cotton.

G. T. M.

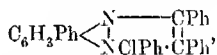
Transformation of *s*-Phenyldiphenylhydrazine by Hydrogen Chloride in Benzene Solution. MIECISLAS DZIURZYŃSKI (*Dokl. Acad. Sci. Cracow*, 1908, 401—408).—When *s*-phenyldiphenylhydrazine is dissolved in benzene and the solution saturated with hydrogen chloride, intramolecular change takes place with formation of a semidine base and a diphenylene base, which are separated by means of their different solubilities in aqueous alcohol.

The semidine base, which is probably 3-amino-4-anilino-diphenyl,



crystallises in silvery scales, m. p. 141°. The acetyl derivative forms white needles, m. p. 165°. The hydrochloride and the sulphate are described. With nitrous acid, the base yields an azimino-derivative,

$\text{NPh} \begin{smallmatrix} \text{C}_6\text{H}_3\text{Ph} \\ \text{N}_2 \end{smallmatrix}$, m. p. 82.5°, with benzil a compound,



of which the free base gives a yellowish-green fluorescence in alcoholic solution, and with carbon disulphide a compound, $\text{C}_6\text{H}_3\text{Ph} \begin{smallmatrix} \text{NH} \\ \text{NPh} \end{smallmatrix} \text{CS}$, yellowish-white scales, m. p. 150°.

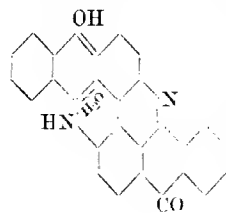
The diphenylene base, which is probably 2:4'-diamino-*p*-diphenylbenzene, $\text{NH}_2 \cdot \text{C}_6\text{H}_3\text{Ph} \cdot \text{C}_6\text{H}_3 \cdot \text{NH}_2$, is a dark oil, crystallising after some months. The diacetyl derivative forms small, hard crystals, m. p. 223°.

The dihydrochloride is blue, and the sulphate crystallises from alcohol in white needles. In the filtrate from the precipitated bases, 4-benzeneazodiphenyl was recognised.

J. C. C.

Indanthren and Flavanthren, X. Products of Reduction of Flavanthren and the Relation between their Colour and Constitution. ROLAND SCHÖLL (*Ber.*, 1908, 41, 2304—2328. Compare Abstr., 1907, i, 540).—By the reduction of flavanthren, the author has prepared seven compounds, namely, dihydroflavanthren, α - and β -tetrahydroflavanthrens, α - and β -hexahydroflavanthrens, flavanthrine, and flavanthrinol, of which the fourth and the last will be described in a later paper.

[With KARL HOLDERMANN.]—*Dihydroflavanthren hydrate* is prepared by reducing flavanthrene with alkaline sodium hyposulphite in an atmosphere of hydrogen. On cooling, bronzy needles of the disodium

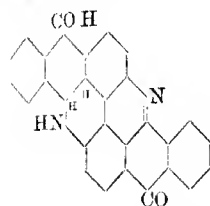


salt (annexed formula, in which the OH and H₂O groups are replaced by ONa and NaOH respectively) crystallise out, and are treated with acetic acid. Dark bluish-green, coppery crystals are obtained, which are fairly stable at the ordinary temperature, but are readily oxidised to flavanthren at 100°, or when moist; when heated for a few hours at 150—170° in a stream of carbon dioxide, water is lost and *dihydroflavanthren* is formed. This

is a green powder, which is not so readily oxidised by the air as is the hydrate. It is also the chief product when flavanthren is heated with hydriodic acid and red phosphorus at 125°. Although flavanthren is of a very weakly basic character, dihydroflavanthren hydrate readily forms salts with mineral acids. *Dihydroflavanthren hydrochloride* probably contains the acid united with the nitrogen atom.

o-Benzoyldihydroflavanthren is a reddish-brown powder, m. p. 220° (decomp.).

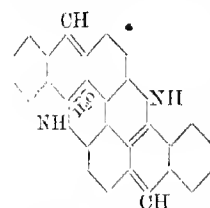
α-Tetrahydroflavanthren hydrate could not be isolated, but the sodium salt is stated to be formed when flavanthren is reduced by zinc dust and sodium hydroxide. On acidification, a mixture of dihydro-



flavanthren hydrate with a small amount of *α*-hexahydroflavanthren hydrate results.

β-Tetrahydroflavanthren (annexed formula), prepared by treating flavanthren with hydriodic acid and red phosphorus at 170°, is a green powder. It forms salts with acids and alkalis, in the latter case passing into the red enolic modification. The *dibenzoyl* derivative forms microscopic, lemon-yellow prisms. The authors consider that *β*-hexahydroflavanthren

is formed when the red alkaline solution of *β*-tetrahydroflavanthren is reduced with zinc dust, but the compound could not be isolated from the resulting yellow solution. By reducing



flavanthren with hydriodic acid and red phosphorus at 207–210°, *flavanthrine hydrate*, annexed formula, is formed as a greenish-brown powder, which on heating to 240° loses water and yields *flavanthrine*. This forms large, brown needles with a green, metallic lustre, and sinters at 380°, m. p. about 390°. It is readily oxidised to flavanthren.

The relation between the colour and constitution of these reduction products of flavanthren is discussed.

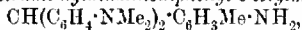
J. C. C.

Influence of Methyl Groups on the Tinctorial Properties of the Basic Dyes derived from Triphenylmethane. JEAN BIELECKI and ALEXANDRE KOLENIEW (*Bull. Acad. Sci. Cracov*, 1908, 296–318).—It is well known that the presence of such substituents as SO_3H , Cl , Br , NO_2 , OH , and CO_2H in the ortho-position to the methane-carbon atom of basic triphenylmethane dyes belonging to the malachite-green and magenta series renders them more resistant towards alkalis. The authors have now examined the effect of introducing the methyl group, not only in the ortho-position (where any increased fastness to alkalis might be assigned to steric hindrance of the change of the quinonoid to the carbinol structure under the influence of alkalis), but also in the meta- and para-positions to the methane carbon-atom. It is found that, in all three positions, the presence of the methyl group increases the fastness to alkalis, whilst with regard to the shade produced, its influence is similar to

that exerted by the acidic groups cited above; in the meta-position no change in colour is evident, whilst in the ortho- and para-positions the change is marked; thus *o*-methylated malachite-green is bluish-green and the *p*-methylated derivative is yellowish-green.

The dyes were prepared by condensing tetramethyldiaminodiphenylcarbinol with 1 mol. of an amine (mostly homologues of dimethylaniline). When the operation is effected in presence of dilute hydrochloric acid, the amine usually attaches itself to the methane carbon atom at the position para to the amino-group, but when concentrated sulphuric acid is used, the point of union is in the meta-position (compare Noelting, Abstr., 1892, 187).

4-Amino-4':4''-tetramethyldiaminodiphenyl-*o*-tolylmethane,



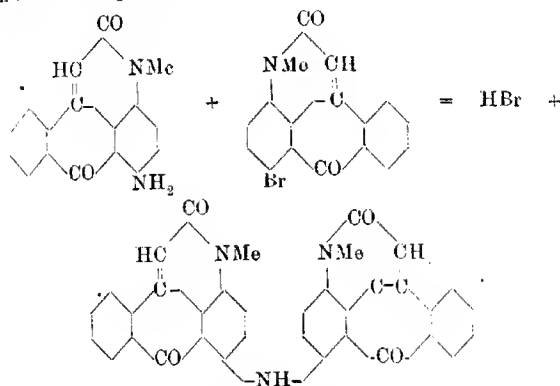
prepared by condensing the carbinol with *o*-toluidine in dilute hydrochloric acid, has m. p. 184°, and is readily oxidised to a dye, which dyes tannin-mordanted cotton in violet-blue shades. When sulphuric acid is used as condensing agent, there is formed 3-amino-4':4''-tetramethyldiaminodiphenyl-*o*-tolylmethane, m. p. 146°, which on oxidation yields a green dye. 4:4':4''-Hexamethyltriaminodiphenyl-*o*-tolylmethane, prepared from dimethyl-*o*-toluidine by condensing it with the carbinol in dilute hydrochloric acid, separates from ether as a pale yellow, microcrystalline powder, m. p. 144°. On oxidation, it yields a violet-blue dye. When sulphuric acid is used as the condensing agent, 3:4':4''-hexamethyltriaminodiphenyl-*o*-toluidine, m. p. 113°, is obtained, which on oxidation gives a yellowish-green dye.

4:4':4''-Hexamethyltriaminodiphenyl-*m*-tolylmethane is prepared by condensing the carbinol with dimethyl-*m*-toluidine in presence of either dilute hydrochloric or concentrated sulphuric acid. It crystallises from methyl alcohol in colourless prisms, m. p. 118°, and on oxidation yields a violet-blue dye. 2:4':4''-Hexamethyltriaminodiphenyl-*p*-tolylmethane, prepared from the carbinol, dimethyl-*p*-toluidine, and dilute hydrochloric acid, crystallises from methyl alcohol in pale yellow flocks, m. p. 107°. The corresponding dye is violet-blue. When 100% sulphuric acid is used as the condensing agent, 3:4':4''-hexamethyltriaminodiphenyl-*p*-tolylmethane, white prisms, m. p. 113°, is obtained (Noelting, Abstr., 1892, 190, gives 100°). The corresponding dyo is bluish-green (compare L. Cassella & Co., Abstr., 1904, i. 804).

2:4':4''-Hexamethyltriaminodiphenyl-*m*-xylylmethane, prepared by condensing the carbinol with dimethyl-*m*-4-xylylidine in dilute hydrochloric acid, crystallises from methyl alcohol in yellow flocks, m. p. 115°. The corresponding dye is blue. When 100% sulphuric acid is the condensing agent, 3:4':4''-hexamethyltriaminodiphenyl-*m*-xylylmethane, prisms, m. p. 135°, is obtained. The corresponding dye is greenish-blue. 4:4':4''-Hexamethyltriaminodiphenyl-*p*-xylylmethane is prepared from the carbinol and dimethyl-*p*-xylylidine by the aid of either dilute hydrochloric or 100% sulphuric acid. It crystallises from methyl alcohol in long needles, m. p. 150°. The corresponding dye is violet-blue. 2:4':4''-Hexamethyltriaminodiphenyl-*o*-xylylmethane, prepared from the carbinol and dimethyl-*o*-4-xylylidine in presence of dilute hydrochloric acid, has m. p. 164°. This base could not be oxidised

either by tetrachloro-*p*-benzoquinone or lead peroxide. 3:4':4"-*Hexamethyltriaminodiphenyl-o-xylylmethane* is obtained when 100% sulphuric acid is used as the condensing agent in the preceding reaction. It crystallises from methyl alcohol in leaflets, m. p. 185°. The corresponding dye is deep blue. J. C. C.

Preparation of Anthracene Derivatives Containing Nitrogen.
FABRIK FÄRBERG VORM. FRIEDR. BAYER & Co. (D.R.-P. 194253. Compare this vol., i, 456).—By condensing 1:4-aminoanthrapyridone with 4-bromoanthrapyridone by means of dry sodium acetate and copper chloride in the presence of naphthalene, a compound crystallising in dark violet needles is obtained, which is formed in accordance with the following equation:



A similar compound containing one anthrapyridone and one anthraquinone residue is obtained by condensing 1:4-bromoanthrapyridone and 4-aminoanthraquinone. Several substances of the same type are described in the patent. G. T. M.

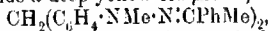
Constitution and Colour. FRIEDRICH KEHRMANN (*Ber.*, 1908, 41, 2340—2345).—Partly a criticism of Willstätter and Piccard's views as to the constitution of Wurster's dyes (this vol., i, 475). The author shows that change of colour can take place in two ways, namely, (1) without change in constitution of the chromophoric group: this occurs when an auxochromic group is introduced; and (2) accompanied by change in constitution of the chromophore, as when colourless bases yield coloured salts and *vice versa*. Quinhydrones are more strongly coloured than quinones, owing to the presence of the auxochromic hydroxyl group, and the compounds to which Willstätter and Piccard have assigned a special constitution do not differ in kind, but only in degree, from ordinary quinhydrones, and are therefore to be regarded as having a constitution similar to these. J. C. C.

Dihydrazines. I. 4:4'-Bismethylhydrazinodiphenylmethane, a Reagent for the Characterisation of Aldehydes. JULIUS VON BRAUN (*Ber.*, 1908, 41, 2169—2181).—4:4'-Bismethylhydrazinodiphenylmethane, obtained by reducing dinitrosodimethyldiaminodiphenylmethane (Braun and Kayser, *Abstr.*, 1904, i, 687) with zinc and acetic acid, reacts instantly with aliphyl and aryl aldehydes, forming condensation products which are readily characterised. It reacts very slowly with ketones, so that a convenient method is afforded of distinguishing between the two. An exception to this rule is displayed by α -keto-carboxylic acids, which react as if they were aldehydes. Aldehydic sugars, such as mannose and galactose, condense immediately, but dextrose reacts only very slowly.

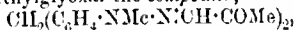
4:4'-Bismethylhydrazinodiphenylmethane, $\text{CH}_3(\text{C}_6\text{H}_4\cdot\text{NMe}\cdot\text{NH})_2$, has m. p. 102° ; the hydrochloride, m. p. 190° (decomp.), and sulphate are described. The semicarbazide, $\text{CH}_3(\text{C}_6\text{H}_4\cdot\text{NMe}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2)_2$, is a white powder, m. p. 232° ; the phenylthiosemicarbazide has m. p. 211° , and the benzoyl derivative softens at 176° and has m. p. 181° .

4:4'-Bismethylhydrazinodiphenylmethane condenses to hydrazones of the type $\text{CH}_3(\text{C}_6\text{H}_4\cdot\text{NMe}\cdot\text{N}\cdot\text{CH}\cdot\text{R})_2$ with the following aldehydes, the figures in brackets being the m. p.: formaldehyde (137°), acetaldehyde (114°), butaldehyde (71°), heptaldehyde (57°), citral ($107\text{--}108^\circ$), benzaldehyde (220° , softening at 214°), cinnamaldehyde (169°), anisaldehyde (195°), *p*-dimethylaminobenzaldehyde (209°), salicylaldehyde (200° with previous sintering), opianic acid (220°), cinnamaldehyde (203°), furfuraldehyde (201°).

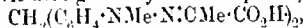
Acetophenone yields a deep yellow compound,



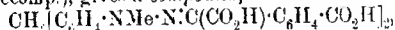
m. p. 105° ; the compound from benzophenone is deep yellow, sintering at 120° , m. p. 152° ; glyoxal yields a compound, $\text{C}_{17}\text{H}_{18}\text{N}_4$, decomp. $280\text{--}282^\circ$, and methylglyoxal the compound,



m. p. 185° . Pyruvic acid gives a yellow compound,



m. p. 100° (decomp.), and phenylpyruvic acid behaves similarly. Phthalonic acid, the phenylmethylhydrazone of which is yellow and has m. p. 140° (decomp.), gives a compound,



softening at 60° , m. p. 78° , and decomposing at 90° . J. C. C.

Disulphides with Neighbouring Double Linkings. III. EMIL FROMM (*Annalen*, 1908, 361, 302—352. Compare *Abstr.*, 1906, i, 656, 714; 1907, i, 982).—It has been shown that all disulphides with neighbouring double linkings, $\text{X}\cdot\text{CR}\cdot\text{S}\cdot\text{S}\cdot\text{C}\cdot\text{Y}$, are decomposed by alkalis and amines with liberation of sulphur and formation of new compounds. Thus perthiocyanic acid reacts with phenylhydrazine, forming sulphur, phenyldithiourazole, 3-amino-5-thion-1-phenyldihydro-1,2,4-triazole, and anilthiuret. Similarly, the thiurets, $\text{NH}\cdot\text{C}(\text{NH})\cdot\text{S}\cdot\text{C}(\text{NR})\cdot\text{S}\cdot$ react with phenylhydrazine, forming two products, considered to have the formulæ $\text{NHR}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{NHPh}$ and $\text{NHR}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}(\text{NH})\cdot\text{NPh}\cdot\text{NH}_2$.

Fromm and Vetter (Abstr., 1907, i, 982) obtained only one product from the interaction of aniline and phenylthiuret, which was considered to have the formula $\text{NHPh} \cdot \text{CS} \cdot \text{NH} \cdot \text{C}(\text{NH}) \cdot \text{NHPh}$. In continuing the investigation, it has now been found that the action of aromatic amines on thiurets gives rise to two products; thus, with aniline and *p*-tolylthiuret, there are formed phenylguanido-*p*-tolylthiocarbamide, $\text{C}_6\text{H}_5 \cdot \text{N} : \text{C}(\text{SH}) \cdot \text{NH} \cdot \text{C}(\text{NH}) \cdot \text{NHPh}$, and phenyl-*p*-tolylguanidothiocarbamide, $\text{C}_6\text{H}_5 \cdot \text{N} : \text{C}(\text{NHPh}) \cdot \text{NH} \cdot \text{C}(\text{SH}) \cdot \text{NH}$.

The action of aniline or phenylhydrazine on thiurets, which are derived from secondary amines, is found to lead to the substitution of the anilino- or phenylhydrazino-group for the secondary amine residue.

The phenyldithionrazole described by Fromm and Schneider (Abstr., 1906, i, 714) has been re-studied, and in connexion with it a number of new dithiobiurets and their derivatives have been prepared.

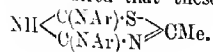
Action of Aromatic Amines and Hydrazines on p-Tolylthiuret.—[With ARNOLD WELLER.]—*p*-Tolylthiuret hydrochloride, $\text{C}_9\text{H}_{10}\text{N}_2\text{S}_2\text{Cl}$, is formed by boiling *p*-tolylthiobiuret with ferric chloride and hydrochloric acid; it is obtained as a yellow, amorphous powder, m. p. 194°, and, when boiled with 2 mols. of aniline in alcoholic solution, forms two products: (a) *Phenylguanido-p-tolylthiocarbamide*, $\text{C}_{15}\text{H}_{16}\text{N}_4\text{S}$, separates from the hot alcoholic solution and crystallises in white leaflets, m. p. 182°. Its *hydrochloride*, $\text{C}_{15}\text{H}_{16}\text{N}_4\text{S} \cdot \text{HCl}$, forms white needles, m. p. 214° (344°). (b) *Phenyl-p-tolylguanidothiocarbamide* is isolated from the alcoholic filtrate as the *hydrochloride*, $\text{C}_{15}\text{H}_{14}\text{N}_4\text{S} \cdot \text{HCl}$, which crystallises in needles, m. p. 158°. When boiled with benzyl chloride and alcoholic sodium hydroxide, the base from (a) yields *phenylguanido-p-tolyl-ψ-benzylthiocarbamide*, $\text{C}_{22}\text{H}_{11}\text{N}_4\text{S}$, which crystallises in white leaflets, m. p. 176°, whereas, under the same conditions, the base from (b) is converted into *phenyl-p-tolylidicyanodiamide*, which crystallises in white leaflets, m. p. 186°.

The action of *p*-toluidine on phenylthiuret leads to formation of only one product, which is identical with the phenyl-*p*-tolylguanidothiocarbamide described above.

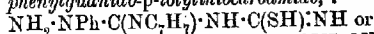
p-Tolylguanido-p-tolylthiocarbamide, $\text{C}_{16}\text{H}_{18}\text{N}_4\text{S}$, formed by the action of *p*-toluidine on *p*-tolylthiuret, crystallises in white needles, m. p. 170–180°; the *ψ*-benzyl derivative forms yellow needles, m. p. 199°.

The arylguanidoarylthiocarbamides are readily acetylated by means of acetic anhydride, whilst the diarylguanidothiocarbamides, on the other hand, do not form acetyl derivatives.

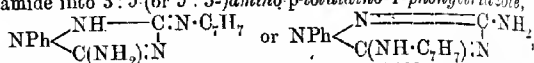
Acetylphenylguanido-p-tolylthiocarbamide, $\text{C}_{17}\text{H}_{18}\text{ON}_4\text{S}$, crystallises in needles, m. p. 225°. When it is heated with sodium hydroxide and benzyl chloride, the latter does not enter into reaction, but the alkali converts the acetyl compound into an *anhydro*-derivative, $\text{C}_{15}\text{H}_{16}\text{N}_4\text{S}$, which crystallises in white needles, m. p. 185°, and when heated with concentrated aqueous sodium hydroxide yields acetic acid and phenylguanido-*p*-tolylthiocarbamide. *Acetyl p-tolylguanido-p-tolylthiocarbamide*, $\text{C}_{18}\text{H}_{20}\text{ON}_4\text{S}$, crystallises in white needles, m. p. 194°. The *anhydro*-derivative, $\text{C}_{15}\text{H}_{18}\text{N}_4\text{S}$, forms needles, m. p. 206°. It is considered that these *anhydro*-derivatives have the constitution



Action of Phenylhydrazine on p-Tolylthiuret.—When treated with 2 mols. of phenylhydrazine, *p*-tolylthiuret hydrochloride yields *aminophenylguanido-p-tolylthiocarbamide*.



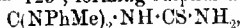
$\text{NH}_2\cdot\text{NPh}\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{C}(\text{NC}_6\text{H}_5)_2\cdot\text{SH}$, which crystallises in white leaflets, m. p. 168°, and forms a *benzylidene* derivative, $\text{C}_{22}\text{H}_{21}\text{N}_3\text{S}$, greenish-yellow powder, decomp. 110°. Alcoholic sodium hydroxide converts aminophenylguanido-*p*-tolylthiocarbamide into 3:5 (or 5:3)-*amino-p-toluidino-1-phenyltriazole*,



which crystallises in white needles, m. p. 148°, is stable towards boiling acids or alkalis, and forms crystalline salts with acids. The *hydrochloride*, $\text{C}_{15}\text{H}_{13}\text{N}_5\cdot\text{HCl}$, white needles, m. p. 172°. The *acetyl* derivative, $\text{C}_{17}\text{H}_{15}\text{ON}_5$, m. p. 115°.

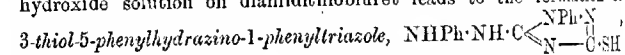
Action of Aromatic Amines and Hydrazines on Phenylmethylthiuret and Phenylethylthiuret.—[With H. BAUMHAUER.]—*Phenylethylthiobiuret*, $\text{C}_{10}\text{H}_{13}\text{N}_3\text{S}_2$, formed by heating perthiocyanic acid with ethyl-aniline, separates from alcohol in crystals, m. p. 119.5°, and when boiled with dilute hydrochloric acid and ferric chloride yields *phenylethylthiuret hydrochloride*, $\text{C}_{10}\text{H}_{11}\text{N}_3\text{S}_2\cdot\text{HCl}$, m. p. 230°.

When boiled with aniline in alcoholic solution, phenyl-, methyl-, or phenylethyl-thiuret yields phenylguanidophenylthiocarbamide, sulphur, and methyl- or ethyl-aniline. Methylphenylthiuret reacts with methylaniline at 120—125°, forming sulphur and the compound,

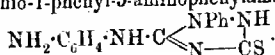


m. p. 90°, which cannot be benzylated with benzyl chloride and sodium hydroxide, but forms lead sulphide when heated with sodium plumbate.

When boiled with 2 mols. of phenylhydrazine, phenylmethylthiuret yields sulphur, methylaniline, 3-amino-5-thiol-1-phenyltriazole, m. p. 234°, and *dianildithiobiuret*, $\text{NH}(\text{CS}\cdot\text{NH}\cdot\text{NHPh})_2$, which crystallises from alcohol in needles, m. p. 178°. The action of cold potassium hydroxide solution on dianildithiobiuret leads to the formation of



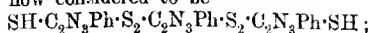
which forms yellowish-red crystals, m. p. 177°, and is oxidised by sulphur in boiling alkaline, or by iodine in boiling alcoholic, solution, forming the *benzeneazotriazole*, $\text{NPh}\cdot\text{N}\cdot\text{C}_2\text{N}_3\text{Ph}\cdot\text{SH}$, which is obtained in brownish-red crystals, m. p. 218°, and is soluble in aqueous alkalis. The action of acetic anhydride on dianildithiobiuret leads to the formation of a *substance*, which has m. p. 218°, but is not identical with the preceding azo-compound, as when boiled with aqueous potassium hydroxide and reprecipitated by an acid it yields the hydrazino-compound, m. p. 177°. When boiled with hydrochloric acid dianildithiobiuret yields the preceding azo-compound, m. p. 218° and a *base*, $\text{C}_{14}\text{H}_{13}\text{N}_5\text{S}$, which crystallises in white needles, m. p. 180.5° and is probably 3-thio-1-phenyl-5-aminophenylaminotriazole,



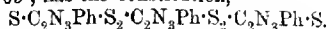
This forms a diacetyl derivative, $C_{18}H_{17}O_2N_3S$, crystallising in colourless needles, m. p. 106° , and a *dibenzylidene* derivative, $C_{28}H_{21}N_3S$, m. p. 195° .

The action of phenylhydrazine on phenylmethyldithiobiuret in boiling alcoholic solution leads to the formation of 3-amino-5-thiol-1-phenyltriazole, m. p. 244° , and 3:5-dithiol-1-phenyltriazole, m. p. 193° .

Oxidation Products of 3:5-Dithiol-1-phenyltriazole.—[With H. BAUMHAUER.]—The oxidation of 3:5-dithiol-1-phenyltriazole by means of iodine in alcoholic solution leads to the formation of two products: the one, m. p. 181° , previously (Abstr., 1906, i, 714) given as $C_{10}H_{10}N_6S_4$, is now considered to be



the other, m. p. 163° , has the constitution,



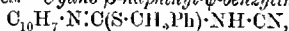
Both oxidation products, when boiled with alkalis, yield the parent dithiolphenyltriazole and small amounts of 3-(or 5)-thiol-1-phenyltriazole, $C_8H_8S_2Ph$, which crystallises in colourless needles, m. p. 178° , and forms a *benzyl* derivative, $C_{15}H_{13}N_3S$, m. p. 64° .

New Dithiobiurets and their Derivatives.—[With A. WELLER.]— β -Naphthylthiobiuret, $C_{12}H_{11}N_3S_2$, formed from perthiocyanic acid and β -naphthylamine, is obtained as a white powder, m. p. 245° .

Dimethylaminophenylthiobiuret hydrochloride, $C_{10}H_{14}N_4S_2HCl$, formed from perthiocyanic acid and aminodimethylaniline, crystallises in white needles, m. p. 205° . The free base forms yellow needles, m. p. 168 — 169° .

β -Naphthylthiuret hydrochloride, $C_{12}H_{10}N_3S_2Cl$, formed by boiling the dithiobiuret with ferric chloride and hydrochloric acid, separates from dilute hydrochloric acid in crystals, m. p. above 300° . *Dimethylaminophenylthiuret hydriodide*, $C_{10}H_{12}N_4S_2 \cdot 2HI \cdot C_2H_5O$, formed by adding iodine to the dithiobiuret in alcoholic solution, crystallises in yellow needles, decomp. 175° .

Formation of Cyanoamides.—The action of benzyl chloride and sodium hydroxide on dithiobiurets leads to the formation of cyano- ψ -benzylthiocarbamides. *Cyano- β -naphthyl- ψ -benzylthiocarbamide*,



crystallises in white leaflets, m. p. 201° . *Cyanodimethylaminophenyl- ψ -benzylthiocarbamide*, $C_{17}H_{15}N_4S$, formed from dimethylaminophenylthiobiuret, crystallises in white needles, m. p. 193° . Cyano-*p*-tolyl- ψ -benzylthiocarbamide (Abstr., 1906, i, 656) is now found to be formed when *p*-tolylthiobiuret is heated with benzyl chloride and concentrated ammonia added.

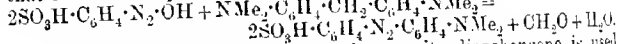
G. Y.

Preparation of Hydroxyalkyl Derivatives of Xanthins Bases. FABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 193799. Compare this vol., i, 475).—The xanthine bases condense with alkylene oxides to form hydroxyalkyl derivatives. 1:3-Dimethyl-7-hydroxyethylxanthine is thus obtained by heating theophylline and ethylene oxide at 150° . Dehydrating agents, such as zinc or hydrogen chloride, may be employed, and theobromine, 3-methylxanthine, and other bases may be similarly condensed with propylene and trimethylene oxides.

G. T. M.

Physico-chemical Researches on the Behaviour of Urates in Solution. F. GUDZENT (*Zeitsch. physiol. Chem.*, 1908, 56, 150—179).—Urates, in which both acidic hydrogen atoms are replaced by a metal, are hydrolysed in solution to monatomic salts; of these, monosodium urate crystallises with $11\text{H}_2\text{O}$, and monopotassium and monoammonium urate crystallise anhydrous. On continued shaking, the amount of these salts dissolved passes through a maximum, and then diminishes somewhat, this ultimate diminution being 4—5 times greater for the ammonium salt than for the sodium and potassium salts. The diminution is not explicable, and is not due to hydrolysis or to a change in size of the particles, or to hydration of the excess of solid salt with which the solution is shaken. The maximum solubilities are: 1 part of potassium, of sodium, and of ammonium urate requires respectively at 18° , 653, 1201, and 2415, and at 37° , 370, 665, and 1352 parts of water. G. B.

Position of Entrance of the Diazo-group in the Formation of Azo-dyes. WASSILI SCHARWIN and KALJANOFF (*Ber.*, 1908, 41, 2056—2060).—The rule that the diazo-group enters the ortho position in a para-substituted amino or phenol does not always hold good. Thus, when the auxochrome is a dialkylamino-group, either no combination takes place (probably owing to steric hindrance) or the *p*-substituent is displaced with formation of the corresponding dye. The authors show that when *p*-diazobenzenesulphonic acid acts on dimethyl-*p*-toluidine, *p*-bromodimethylaniline, dimethylsulphanilic acid, *p*-dimethylaminodiphenylmethane, tetramethylbenzidine, or *N*-dimethyl- β -naphthylamine, no dye is formed. *N*-Dimethyl- β -naphthylamine, as was to be expected, forms 4-*p*-sulphobenzeneazo-1-dimethylnaphthylamine, $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_7\cdot\text{NMe}_2$, crystallising from water in violet, glistening needles. The sodium salt forms golden-yellow leaflets. The authors confirm Pinnow's observation (*Abstr.*, 1895, i, 98) that helianthin is formed when diazobenzene sulphonic acid acts on tetramethyldiaminodiphenylmethane, and show that the reaction proceeds according to the equation



A similar reaction takes place when *p*-nitrodiazobenzene is used (compare Noetting, *Abstr.*, 1888, 270; Bamberger, *Abstr.*, 1895, i, 351).

When diazobenzenesulphonic acid acts on *p*-dimethylaminobenzole acid, the carboxyl group is eliminated and helianthin is formed (compare Limpricht, *Abstr.*, 1891, 1036) without any other product (compare Grandmougin and Freimann, *Abstr.*, 1907, i, 956). By treating *m*-phenylenetetramethyldiamine with diazobenzenesulphonic acid, 4-*p*-sulphobenzeneazo-*m*-phenylenetetramethyldiamine (Pinnow and Wegner, *Abstr.*, 1898, i, 185) was prepared. This forms microscopic, Bordeaux-red needles; the alkali salts are orange coloured. J. C. C.

Ethyl Arylazoacetateacylhydrazones and their Conversion into Derivatives of 4-Arylazo-3-methyl-5-pyrazolones with an Acid Radicle Attached to the Primary Nitrogen Atom. CARL BÜLOW and FRIEDRICH SCHAUB (*Ber.*, 1908, 41

2355—2366. Compare Abstr., 1907, i, 301; this vol., i, 579; Curtius, Darapsky, and Müller, Abstr., 1907, i, 451).—A number of

4-arylaazo-1-acyl-3-methylpyrazolones, $\text{COR}\cdot\text{N} \begin{smallmatrix} \text{N}=\text{CMe} \\ \text{CO}\cdot\text{CH}\cdot\text{N}_2\text{R}' \end{smallmatrix}$, have

been prepared from 1:2-acylhydrazones of ethyl arylazoacetoacetates, $\text{COR}\cdot\text{NH}\cdot\text{N}:\text{CMe}\cdot\text{CH}(\text{N}_2\text{R}')\cdot\text{CO}_2\text{Et}$. Contrary to the statements of Curtius and Struve (Abstr., 1893, i, 34), therefore, pyrazolones can be formed from the acylhydrazones of α -substituted ethyl acetoacetates. On hydrolysis, the acyl-pyrazolone yields the corresponding 4-arylaazo-

3-methyl-5-pyrazolone, $\text{NH} \begin{smallmatrix} \text{N}=\text{CMe} \\ \text{CO}\cdot\text{CH}\cdot\text{N}_2\text{R}' \end{smallmatrix}$, which can be synthesised from the ethyl arylazoacetoacetates, $\text{COMe}\cdot\text{CH}(\text{N}_2\text{R}')\cdot\text{CO}_2\text{Et}$.

The benzoylhydrazones of ethyl arylazoacetoacetates are formed from the ethyl arylazoacetoacetate and benzoylhydrazide in cooled acetic acid solution, and can be recrystallised only under certain conditions, as intramolecular ring condensation, followed in some cases by fission of the benzoyl group, takes place with great ease.

The benzoylhydrazone of ethyl phenylazoacetoacetate, $\text{C}_{19}\text{H}_{20}\text{O}_3\text{N}_4$, crystallises in canary-yellow needles, m. p. 156°, and, when dissolved in cold dilute alkali hydroxides and precipitated immediately by means of carbon dioxide, is regained unchanged. When heated with aqueous sodium hydroxide or acetate on the water-bath, it condenses to 4-benzeneazo-3-methyl-5-pyrazolone, $\text{C}_{16}\text{H}_{16}\text{ON}_4$, which crystallises in orange-red leaflets, m. p. 199.5—200° (197°: Rothenburg, 1895, i, 686).

Ethyl *o*-tolylazoacetoacetate, $\text{C}_{13}\text{H}_{12}\text{O}_3\text{N}_2$, formed by the action of diazotised *o*-toluidine on ethyl acetoacetate in presence of sodium acetate, crystallises in lemon-yellow needles, m. p. 67°. The benzoylhydrazone crystallises in yellow needles, m. p. 145—149°, and on recrystallisation forms 4-*o*-tolueneazo-3-methylpyrazolone, $\text{C}_{11}\text{H}_{12}\text{ON}_4$, orange leaflets, m. p. 224—225°, and its 1-benzoyl derivative, $\text{C}_{15}\text{H}_{16}\text{O}_3\text{N}_4$, scales, m. p. 209°.

The benzoyl derivative of ethyl *p*-tolylazoacetoacetate, formed from diazotised *p*-toluidine and ethyl acetoacetate, crystallises in yellow needles, m. p. 165°. 4-*p*-Tolueneazo-3-methyl-5-pyrazolone forms orange leaflets, m. p. 196°.

Ethyl *m*-xylylazoacetoacetate, $\text{C}_{14}\text{H}_{12}\text{O}_3\text{N}_2$, crystallises in yellow needles, m. p. 121°. The benzoylhydrazone, $\text{C}_{21}\text{H}_{22}\text{O}_3\text{N}_4$, m. p. 145—149°. 4-*m*-Xyleneazo-1-benzoyl-3-methyl-5-pyrazolone, $\text{C}_{19}\text{H}_{18}\text{O}_3\text{N}_4$, orange-red needles, m. p. 171—172°. 4-*m*-Xyleneazo-3-methyl-5-pyrazolone, $\text{C}_{12}\text{H}_{14}\text{ON}_4$, m. p. 190—191°.

The benzoylhydrazone of ethyl α -naphthylazoacetoacetate, $\text{C}_{25}\text{H}_{22}\text{O}_3\text{N}_4$, forms brownish-yellow threads, m. p. 165—167° (decomp.). 4- α -Naphthaleneazo-1-benzoyl-3-methyl-5-pyrazolone, $\text{C}_{21}\text{H}_{18}\text{O}_3\text{N}_4$, yellowish-red needles, m. p. 212°. 4- α -Naphthaleneazo-3-methyl-5-pyrazolone, $\text{C}_{14}\text{H}_{12}\text{ON}_4$, brownish-red crystals, m. p. 247°.

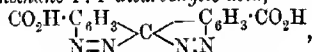
The benzoylhydrazone of ethyl β -naphthylazoacetoacetate, $\text{C}_{25}\text{H}_{22}\text{O}_3\text{N}_4$, forms canary-yellow crystals, m. p. 160—164° (decomp.). 4- β -Naphthaleneazo-1-benzoyl-3-methyl-5-pyrazolone, $\text{C}_{21}\text{H}_{18}\text{O}_3\text{N}_4$, orange crystals, m. p. 224°. 4- β -Naphthaleneazo-3-methyl-5-pyrazolone forms

red crystals, m. p. 237—238°, and yields a *sodium* salt, which is decomposed by carbon dioxide or boiling alcohol.

Ethyl carboxyphenylazoacetoacetate, $C_{13}H_{14}O_5N_2$, formed from diazotised anthranilic acid, is obtained in yellow crystals, m. p. 162—163°. The *benzoylhydrazone*, yellow crystals, m. p. 244—245°. *4-Carboxybenzenazo-3-methyl-5-pyrazolone*, $C_{11}H_{10}O_5N_4$, crystallises in orange needles, m. p. above 280° (decomp.). G. Y.

Bisazo-compounds. HENRI DUVAL (*Compt. rend.*, 1908, 146, 1407—1409).—Continuing his recent work (Abstr., 1907, i, 663), the author finds that nitrous acid acts on the di-*o*-amino-derivatives of diphenylmethane-4:4'-dicarboxylic acid, of 4:4'-dicyanodiphenylmethane, and of 4:4'-diacetyldiphenylmethane to produce bisazo-compounds, whilst with the di-*o*-amino-derivatives of diphenylmethane and of 4:4'-diacetyldiaminodiphenylmethane, nitrous acid gives a mixture of the corresponding phenol and the bisazo-compound.

Bisazodiphenylmethane-4:4'-dicarboxylic acid,



can be obtained by hydrolysing its ethyl ester (*loc. cit.*), but is best prepared as described above. It melts above 300°. 4:4'-*Dicyano-bisazodiphenylmethane* melts above 350°. 4:4'-*Diacetylbisazodiphenylmethane* separates from pyridine in bright yellow crystals, decomp. at about 300°. 4:4'-*Diacetyldiaminobisazodiphenylmethane* forms red crystals, m. p. above 300°. The conclusion is drawn that the presence of an electronegative substituent in the diphenylmethane nucleus favours the formation of bisazo-compounds of the above type.

J. C. C.

Aminoazo-compounds. ARTHUR HANTZSCH (*Ber.*, 1908, 41, 2435—2437).—Reply to Hewitt (this vol., i, 581). C. S.

Protein Constitution. New Method of Hydrolysis by Means of Hydrofluoric Acid. L. HUGOUNEQ and ALBERT MOREL (*Compt. rend.*, 1908, 146, 1291—1293).—It is claimed that hydrofluoric acid is superior to other acids as a reagent for the hydrolysis of proteins. Far less of the humin substances are formed; the acid can be readily removed after completion of the reaction by calcium carbonate, and the amino- and diamino-acids formed can be obtained in a state of great purity. Commercial hydrofluoric acid (50%) diluted with about five times its volume of water is employed. The mixture with proteins is heated in lead vessels on a water-bath for from forty-eight to one hundred hours, until the biuret reaction disappears. S. B. S.

Calorimetric Investigation on Protein Precipitation. AMEDEO HERLITZKA (*Biochem. Zeitsch.*, 1908, 11, 481—492).—During the process of salting-out protein with ammonium sulphate, or during the converse process of re-solution due to dilution, there is no development of heat. In the precipitation process, only protein, and not any salt, is precipitated. In precipitation with silver nitrate, the precipitate

contains both protein and silver, and heat is developed. If, however, the precipitate contains much silver, heat production is negative, due to adsorption of silver by the protein. The heat developed is 4.18 calories per gram of protein. If adsorption occurs, the calorific value is -16.67 cal. per gram of silver nitrate. W. D. H.

The Diffusion of Colloids. II. REGINALD O. HERZOG and H. KASARNOWSKI (*Biochem. Zeitsch.*, 1908, 11, 172—176).—The diffusion coefficients of various colloidal substances were determined. The coefficient can be regarded as a physical constant. By its means it can be determined whether a given product is a mixture; trypsin, for example, was found to consist of a mixture of ferments. By means of the diffusion constant, from the equation $M = 59.2/K^2$, the molecular weight of a solution can be determined.

The results agree well with those obtained by other methods. For ovalbumin, the molecular weight found was 17,000; for ovomucoid, 30,000; for pepsin, 13,000; for invertin, 54,000, and for emulsin, 45,000. S. B. S.

The Influence of Temperature on the Co-aggregation of Colloids. BERTRAM H. BUXTON and ALFRED H. RAHE (*Beitr. chem. Physiol. Path.*, 1908, 11, 479—501).—The different colloids were mixed with dye solutions, chiefly night-blue and Janus-green, and the concentration was noted at which co-aggregation of the colloids most readily took place at temperatures between 0° and 80°. In the case of negative organic colloids, it was found that the higher the temperature the greater the quantity of dye necessary to produce co-aggregation. The increased quantities necessary when the temperature is raised are much greater in the case of reversible colloids than in that of irreversible colloids. These phenomena are absent in the case of inorganic colloids.

When basic hydroxides are used to produce co-aggregation of negative organic colloids, instead of dyes, the quantity is independent of temperature. Mastic appears to be an exception to this rule.

Experiments were also made by transferring the mixtures, after the co-aggregation phenomena had been observed at a particular temperature, to higher and lower temperatures, with the object of studying reversion of the phenomena. By increasing the temperature, it was found that the type that was characteristic at the lower temperature was converted into the type characteristic for the higher. Lowering the temperature did not, however, alter the type. S. B. S.

Changes in the Physical State of Colloids. VI. Compounds of Salt Ions with Amphoteric Protein. WOLFGANG PAULI and HANS HANDOVSKY (*Beitr. chem. Physiol. Path.*, 1908, 11, 415—448).—By amphoteric protein is meant protein which has been subjected to so long a period of dialysis that the product is no longer a salt of either acid or base. For the purposes of the investigation, ox-serum was employed, which had been dialysed against repeatedly-changed carbon dioxide-free water for at least six weeks. To determine the influence of salts on such a protein, the coagulation-tempera-

ture was ascertained in the presence of varying quantities. It was found that both the ions and anions had influence on the coagulation-temperature. The chlorides of potassium, sodium, ammonium, and magnesium give curves of similar form (when the concentrations are plotted as abscissæ, and the coagulation-temperatures as ordinates), which rise at first rapidly and then slowly. The curves given by the alkaline-earth chlorides show a maximum coagulation-temperature when the concentration of the salt reaches $N/2$; after this point there is a fall. The curve for lithium chloride lies between those of the two groups, showing a maximum coagulation point only when the concentration reaches $1N$. The influence of the different anions is very varied. The potassium salts were used in the experiments. Cl, Br, SO_4 , and NO_3 form a group in which additions of salt up to concentrations of 0.5 to $1N$ cause a rise of coagulation-temperature; additions beyond this point up to 1 to $3N$ cause but slight variations. SCN and I act in a similar way up to 0.5 to $1N$; above this point they cause marked inhibition, and potassium thiocyanate in $1N$ solution and potassium iodide in $2N$ solution cause total inhibition.

The inhibition of coagulation can be due to two causes; either a change in the protein, such as the formation of an acid or alkali albumin, or an inhibition of the aggregation of charged particles. To test this point, a protein solution containing potassium thiocyanate in concentration $2N$ was boiled for some minutes, and then divided into two portions; one was kept under toluene, and the other was dialysed; the former remained clear, and the latter gradually deposited coagulated protein. The experiment indicates that the coagulation is inhibited by the salt preventing the aggregation of particles.

It was assumed that proteins in salt solutions form adsorption compounds with salts, and that the formation of such compounds exerts a marked influence on the coagulation-temperature. If this is the case, then $t - t_0 = Kc^m$, where K and m are constants, c the concentration of the salt, and t and t_0 the coagulation-temperatures of protein salt mixture and pure protein solutions respectively. If $\log(t - t_0)$ be plotted as ordinates and $\log c$ as abscissæ, the curve representing the relations between the temperature of coagulation and concentration of the salt should be a straight line. This was the case with several of the salts investigated (up to concentrations of $0.1N$). At higher concentrations, other more complex factors come into play.

The theory of surface adsorption of salt ions by proteins was further tested by the measurement of viscosities. Protein, even in small concentration, considerably increases the internal friction of water, whereas inorganic salts up to concentrations of $0.05N$ have but little influence. If the theory of surface adsorption is correct, the salt ions on the surface of the colloidal protein molecules should mask the influence of the latter on the internal friction. It was found that neutral salts, which by themselves increase the viscosity of pure water, without exception lower the internal friction of amphoteretic protein; in fact, in presence of sodium chloride, thiocyanate, and sulphate, calcium chloride, and potassium thiocyanate in concentrations of 0.01 to $0.05N$ (in which concentrations of the salts alone

the viscosity of water is increased), the viscosity of the protein is lower than that of pure protein solution.

Non-electrolytes, such as sucrose, have but little influence on the coagulation-temperature; they have but little influence also on the internal friction of protein solutions. The case of urea is somewhat exceptional. This substance appears to act chemically on the proteins. The general parallelism between the influence of substances on heat coagulation and internal friction of protein supports generally a conception of adsorption compounds.

The action of alkalis and readily hydrolysed salts, such as aluminium chloride, was investigated. In these cases the conditions are much more complex. S. B. S.

The Formation of Hydrogen Sulphide from Protein and Sulphur. HERMANN HILDEBRANDT (*Beitr. chem. Physiol. Path.*, 1908, 11, 409—410).—Experiments made by precipitating proteins with tannic acid and with mercuric chloride show that the substances which cause precipitation do not always prevent the reducing action of proteins on sulphur. A protein which has been precipitated with tannic acid can cause the reduction of sulphur, whereas one which has been precipitated with mercuric chloride has lost this property. S. B. S.

Complete Hydrolytic Decomposition of Egg-albumin at 180°. P. W. LATHAM (*Biochem. J.*, 1908, 3, 207—240). **The Synthesis of Living Albumin.** P. W. LATHAM (*Biochem. J.*, 1908, 3, 241—257).—Two theoretical papers, consisting of speculations based on the old results of Schützenberger, but without any new experimental facts. It is pointed out how the leucéines and a number of other substances obtained by Schützenberger might be synthesised (in the laboratory) from pyruvic acid. In accordance with Pflüger's view, the death of protoplasm is regarded as consisting in the change $R\cdot CH(OH)\cdot CN \rightarrow R\cdot CH<\overset{NH}{\underset{CO}{\curvearrowright}}$. G. B.

A Modification of the Properties of Gluten produced by Sulphurous Acid. J. DUGAST (*Compt. rend.*, 1908, 146, 1287—1288).—Gluten undergoes a considerable change in its physical properties when treated with sulphurous acid; flour which has been submitted to the fumes of the acid, on this account, loses its value for bread-making. S. B. S.

Action of Reducing Agents on Compounds of Hæmoglobin. BENTKER (*Chem. Zentr.*, 1908, i, 1630; from *Wrtjschr. ger. Med. öffentl. Sanitätswesen.*, 1908, 35, 262—265).—Experiments have been made with ammonium sulphide, sodium hypophosphite, sodium hydrogen sulphite, hydroxylamine hydrochloride, hydrogen sulphide, ferrous tartrate in ammoniacal solution, and stannous chloride. It is found that sodium hydrogen sulphite is as good a reducing agent for blood as hydrogen sulphide or ferrous tartrate, and has the advantage that it does not greatly increase the quantity of blood and gives a clear, colourless solution. J. V. E.

Hæmopyrrole. LEON MARCHLEWSKI and J. RETINGER (*Biochem. Zeitsch.*, 1908, 10, 437—453).—The hæmopyrrole obtained by the reduction of hæmatoporphyrin appears, according to the later researches of Küster, to be a mixture of substances. He succeeded in obtaining by oxidation an imide which was not that of methylpropylmaleic acid, but corresponded more with that of methylmaleic acid. The analyses of the product obtained by the action of diazobenzene chloride on hæmopyrrole (Marchlowski, Goldmann, and Hetper) indicated that hæmopyrrole is a methylpropyl rather than a methyl-ethyl derivative of pyrrole. Further investigations of the action of diazobenzene chlorido on hæmopyrrole have revealed the fact that the product just discussed, with the formula $C_{29}H_{29}N_3Cl$, is accompanied by another crystalline product of ruby red colour, a substance crystallising in green needles, and a third product crystallising in reddish-violet needles.

S. B. S.

The Carbohydrate Group in Nucleic Acid. II. HERMANN STEUDEL (*Zeitsch. physiol. Chem.*, 1908, 56, 212—219. Compare this vol., i, 487).—The proofs that nucleic acid yields a pentose are regarded as insufficient; on theoretical grounds, the carbohydrate is more probably a hexose, and this is supported by experiment. W. D. H.

State of Combination of Sulphur in the Keratin Molecule. OSKAR BAUDISCH (*Chem. Zeit.*, 1908, 32, 620).—With the object of obtaining evidence that the sulphur is in combination with oxygen in the keratin molecule, the author has repeated the experiments of Raikow (Abstr., 1905, i, 725), using wool, and substantiated his results that syrupy phosphoric acid at the ordinary temperature oxidises the sulphur contained to sulphur dioxide. Further, the oxidation of the sulphur of the wool to sulphur trioxide has been effected at the ordinary temperature by means of hydrogen peroxide. When, however, the wool is first chlorinated, no trace of sulphur dioxide is observed when treated with phosphoric acid.

J. V. E.

Phenomena of the "Precipitation" and "Insolubilisation" of Gelatin. AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and ALPHONSE SEYEWETZ (*Bull. Soc. chim.*, 1908, [iv], 3, 743—750. Compare Abstr., 1907, i, 573).—The action of a large number of organic and inorganic substances on gelatin solutions has been examined with a view to ascertaining (1) whether those substances which "precipitate" gelatin or render it "insoluble" have any characters in common, and (2) the nature of the "precipitated" and "insolubilised" gelatins formed.

It is found that in the "precipitation" reactions, two types of products are formed: (a) substances soluble in warm water, which have the properties and composition of the original gelatin; (b) substances insoluble in warm water, in which the properties of the original gelatin have been considerably modified. The first type of product is obtained when (1) concentrated solutions of alkali salts, (2) dilute solutions of phosphotungstic or phosphomolybdic acid, and (3) phenols or substitution products of phenols are added to solutions of gelatin. The second type of product is obtained when substances

capable of furnishing oxygen, directly or indirectly, are added to gelatin solutions, for example, the halogens, ferric salts, uranates, manganates, permanganates, &c. Among organic substances, tannin is the only substance which gives with gelatin a precipitate insoluble in warm water.

Gelatin is "rendered insoluble" but not "precipitated" by chromium salts, and by formaldehyde, quinone, and oxidation products of various polyhydric phenols (compare *Abstr.*, 1906, i, 614, 915, 999; 1907, i, 573).

T. A. H.

Gelatoses. ZDENKO H. SKRAUP and F. HUMMELBERGER (*Monatsh.*, 1908, 29, 451—469).—The hydrolysis of proteins with the object of obtaining albumoses and peptones is usually carried out by means of enzymes or very dilute acids. The authors have now studied the hydrolysis by means of relatively concentrated acid, and have endeavoured to improve the ammonium sulphate method of separating the products. Gelatin was chosen for study in consequence of its solubility in water and acids. The fractions precipitated from the product of hydrolysis by concentrated acid by means of various concentrations of ammonium sulphate were isolated and hydrolysed. Glycine, glutamic acid, arginine, and lysine, which occur in gelatin in large amounts, and histidine were estimated in the product of the hydrolysis of each fraction; other amino-acids, which occur only in small amounts, were not estimated. On complete hydrolysis, gelatin yields the following percentages of cleavage products: glutamic acid, 13.9, estimated by Horbaczewski's method, or 10.1, estimated by Fischer's osterification method; glycine, 9.6, 9.7; histidine, 0.4; arginine, 6.2; lysine, 4.4. Fischer found only 0.9% of glutamic acid, but 16.5% of glycine, and Levene (*Abstr.*, 1907, i, 168), 16.38% of glycine from gelatin.

Whilst gelatin is hydrolysed completely to simple amino-acids by boiling 25% sulphuric acid (Levene, *loc. cit.*), products of partial hydrolysis are obtained with the same acid at 50°. The albumoses, precipitated on partial and on complete saturation of the hydrolysis product with ammonium sulphate, and the peptone fraction, which is soluble in ammonium sulphate and was purified by dialysis, were hydrolysed by boiling concentrated hydrochloric acid, or by boiling dilute hydrochloric acid and stannous chloride. The albumoses precipitated by one-third or by one-half saturation gave the following percentages, *A*, of cleavage products; those precipitated by complete saturation gave the percentages *B*; the peptone solution gave the percentages *C*; and the first solution from the dialysator, the percentages *D*.

	Glutamic acid.		Glycine.	Histidine.	Arginine.	Lysine.
	Fischer's method.	Horbaczewski's method.				
<i>A</i>	2.5	5.8	10.2 10.3	5.8		1.8
<i>B</i>	15	11	6.6 10.5	5.4		2.3
<i>C</i>	29.8		7.2	0.4	6.3	3.8
<i>D</i>	16		4.1	0.3	4.0	4.8

The more soluble the albumose in ammonium sulphate solution the greater its percentage of glutamic acid and histidine, but the smaller

the percentage of glycine. The peptone is distinguished from the albumoses by a high percentage of glutamic acid and small percentage of glycine. G. V.

Preparation of Stable Soluble Compounds of Hexamethylenetetramine Silver Nitrate with Albumoses. ALBERT BUSCH (D.R.P. 193740).—Hexamethylenetetramine silver nitrate combines with albumoses in aqueous solution to form a soluble additive compound containing 8 per cent. of silver, which is obtained as a yellowish-brown powder either on concentrating the solution under reduced pressure or by precipitation with alcohol.

The dry components may also be mixed, and an extract made with 50% alcohol; the product is then obtained by evaporating down this solution. G. T. M.

Studies on Enzyme Action. XI. Hydrolysis of Raffinose by Acids and Enzymes. HENRY E. ARMSTRONG and WILLIAM H. GLOVER (*Proc. Roy. Soc.*, 1908, 80, B, 312—321).—The rate of hydrolysis of raffinose into melibiose and levulose, both by invertase and by acids, was investigated, and compared with the rate of action of the same reagents on sucrose. The rate of hydrolysis of raffinose is considerably smaller than that of sucrose. The influence of the stereochemical configuration on the rate of hydrolysis is discussed. S. B. S.

Physico-chemical Investigation of Amylase and Maltase. Mlle. CH. PHILOCHE (*J. Chim. Phys.*, 1908, 6, 355—423. Compare this vol., ii, 470).—*Action of Amylase on Starch and Glycogen* (continued).—In a solution containing 0.004% of amylase of malt and 2% of starch, hydrolysis is practically complete in eight to nine hours, and even for smaller enzyme concentrations there does not appear to be any interruption of the reaction. On the other hand, a 2% solution of glycogen is completely hydrolysed by a 2% solution of amylase of malt only after twenty-six hours, and in solutions containing less than 1% of the enzyme hydrolysis is incomplete. For solutions containing 0.01 to 0.125% of the enzyme, the proportion of maltose formed is approximately proportional to the enzyme concentration. The stoppage of the reaction is not due to the destruction or weakening of the enzyme, and in such partly hydrolysed solutions the glycogen is no longer present in its original form.

Glycogen is hydrolysed somewhat less rapidly than starch by pancreatic juice, but, as shown above, amylase acts much less rapidly on glycogen than on starch. The rate of reaction between amylase and starch is somewhat complicated; it diminishes fairly rapidly until about 30% of the starch is decomposed, and then proceeds as a unimolecular reaction until hydrolysis is almost complete.

The last part of the paper contains a general discussion of the mechanism of enzyme reactions in the light of all the available accurate data. The reactions take place in heterogeneous systems, and the purely chemical actions are therefore complicated by diffusion and adsorption phenomena (compare Nernst, *Abstr.*, 1904, ii, 315; Henri, *Abstr.*, 1906, ii, 13). G. S.

Organic Chemistry.

Action of Metallic Oxides on the Primary Alcohols (Irreducible Oxides). PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1908, 147, 106—110. Compare this vol., i, 594).—Many metallic oxides, which are not reduced by alcohol vapour, decompose primary alcohols catalytically. The decomposition may be into hydrogen and an aldehyde, as with manganous oxide (and also with stannous and cadmium oxides; these two are, however, slowly reduced); secondly, the decomposition may be a dehydration, alumina, thoria, and blue oxide of tungsten with ethyl alcohol yielding ethylene and water; with a third group of oxides (Cr_2O_3 , SiO_2 , TiO_2 , Ga_2O_3 , ZrO_2 , UO_2 , Mo_2O_3 , V_2O_5 , ZnO), the two reactions first mentioned proceed simultaneously, ethylene and hydrogen appearing together. With certain higher alcohols, complications may arise; thus *isobutyl* alcohol yields a little *diisobutylene*, and *benzyl* alcohol gives a resinous deposit of the composition $(\text{C}_7\text{H}_8)_n$.

The reaction is greatly accelerated by a rise of temperature, in one case being fifteen times as rapid at 350° as at 260° . G. B.

Formation of Compounds in Solutions of Tartaric Acid and Sodium Molybdate. P. QUINET (*Compt. rend.*, 1908, 147, 203—206).—The author has studied certain physical properties of solutions containing a fixed weight of *d*-tartaric acid and varying weights of sodium molybdate. The specific gravity, specific rotatory power, electrical conductivity, and freezing point of each solution have been examined and the results plotted on curves, the abscissæ of which are the weights of sodium molybdate. It is found that the curves exhibit sharply-defined maxima, which correspond in each case with a compound of one molecule of tartaric acid with two molecules of sodium molybdate. The existence of this combination was indicated by Gernez from polarimetric observations (*Abstr.*, 1887, 540). The cryoscopic curve shows a minimum corresponding with a compound containing one molecule of each substance, but the existence of this is not confirmed by the other curves. W. O. W.

Methyl Hydrogen *d*-Tartrate. F. TANNHÄUSER (*Zeitsch. Kryst. Min.*, 1908, 45, 183—184).—The crystals are rhombic [$a:b:c=0.8887:1:0.557$].

L. J. S.

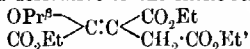
Ketonic Dibasic Acids. EDMOND E. BLAISE and H. GAULT (*Compt. rend.*, 1908, 147, 198—200).—This paper contains a preliminary account of a general method for the preparation of certain new α -monoketonic and $\alpha\alpha'$ -diketonic dibasic acids. When ethyl oxalosuccinate is treated with hydrogen chloride in the cold and the solution boiled, hydrolysis takes place and a *ketoglutaric acid*,

$\text{CO}_2\text{H}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, is formed. This very reactive substance has m. p. $112-113^\circ$.

Ethyl oxalate and ethyl methylsuccinate condense in presence of sodium ethoxide to form *ethyl α -methyl- α -oxalosuccinate*,



which decomposes on distillation. An attempt to prepare the same substance by the action of propyl iodide on ethyl oxalosuccinate led to the formation of a derivative of the enolic form of this ester,



b. p. $202-203^\circ/20$ mm. When treated with hydrogen bromide, this substance yields ethyl bromide, propyl bromide, and α -ketoglutaric acid.

An attempt to prepare *aa'*-diketoglutaric acid by the hydrolysis of ethyl dioxalosuccinate resulted in the formation of *3-hydroxy-2-pyrone-6-carboxylic acid*, $\text{C}_6\text{H}_4\text{O}_5$. This, when heated at 200° , loses carbon dioxide and yields a substance identical with Limpricht's isopropionic acid; thus confirming the constitution ascribed to this compound by Chavanne (Abstr., 1904, i, 77).

W. O. W.

Optically Active Thiolactic Acids and Thiodilactylic Acids.

JOHAN M. LOVÉN (*J. pr. Chem.*, 1908, [ii], 78, 63-73).—Although two inactive thiodilactylic acids were described previously (Abstr., 1896, i, 412) as the racemic and the *meso*-acid respectively, attempts to resolve either into the optically active components by means of the alkaloid salts have been unsuccessful, as was also the employment of the active forms of α -phenylethylamine. Dithiodilactylic acid readily undergoes resolution into its optically active components; these on reduction yield the corresponding optically active thiolactic acids, which on treatment with α -bromopropionic acid in alkaline solution yield the optically active thiodilactylic acids.

i-Thiolactic acid (Abstr., 1884, 1298) is best prepared by reduction of trithiodilactylic acid with sodium amalgam in dilute sulphuric acid solution. On treatment with a ferric salt in acid solution, addition of an excess of potassium carbonate, and exposure to air, it yields a mixture of *r*- and *i*-dithiodilactylic acids. The *r*-acid separates in slender needles on addition of hydrochloric acid to the concentrated aqueous solution of the potassium salts. On treatment of the *r*-acid with *d*- or *l*- α -phenylethylamine in aqueous solution, the *d*-base *d*-acid salt, or the *l*-base *l*-acid salt, $\text{S}_2(\text{CHMe}\cdot\text{CO}_2\text{H})_2\cdot\text{CHPhMe}\cdot\text{NH}_2$, separates in long, glistening needles, the isomeric salt remaining in solution. *d*-Dithiodilactylic acid crystallises in rhombic plates, m. p. 116.5° , $[\alpha]_D^{20} + 42.9^\circ$.

The optically active thiolactic acids are prepared by reduction of *d*- and *l*-dithiodilactylic acids, or their α -phenylethylamine salts, by means of sodium amalgam. *l*-Thiolactic acid, b. p. about $99-101^\circ/15$ mm., $D^{20}_D + 1.193$, $[\alpha]_D^{20} - 45.47^\circ$, closely resembles the *r*-acid. The mercuric derivative, $\text{Hg}(\text{S}\cdot\text{CHMe}\cdot\text{CO}_2\text{H})_2$, was analysed.

The optically active thiodilactylic acids crystallise in large, rhombic prisms, m. p. 117° ; the *l*-acid has $[\alpha]_D - 190.0^\circ$. A solution of the two isomerides deposits the inactive acid, m. p. 125° , crystallising in monoclinic prisms, which is therefore the racemic form (*loc. cit.*). *l*-Thiodi-

lactic acid is formed also by the action of sodium sulphide on *d*-α-bromopropionic acid, the rotatory power being reversed by the substitution of sulphur for bromine. G. Y.

The Fission of Sugars [Sucroclasm]. I. Action of Zinc Carbonate on Formaldehyde Solutions. WALTHER LÖB (*Biochem. Zeitsch.*, 1908, 12, 78—96).—In addition to a number of theoretical arguments, the following experiments are adduced in support of the author's view that alcoholic fermentation does not take place through the intermediate formation of lactic acid, but that it consists in a breaking-down of the sugar to H·C·OH groups, with subsequent synthesis to alcohol and carbon dioxide. By boiling 40% formaldehyde solution with two volumes of 30% potassium hydroxide, there are not only formed methyl alcohol and formic acid, as found by Nef (*Abstr.*, 1905, i, 3), but also non-volatile hydroxy-acids (probably di- and tri-hydroxybutyric acids). By boiling 200 c.c. of 20% formaldehyde solution with 20 grams of zinc carbonate for several days, there are formed, in addition to the above products, acetol, COMe·CH₂·OH, and methylketol, COMe·HCOMe·OH, which are isolated after distillation with steam as osazones. The zinc carbonate does not act as an oxidising agent, since zinc dust has the same qualitative effect. G. B.

Perseulose, a New Crystalline Sugar with Seven Carbon Atoms. GABRIEL BERTRAND (*Compt. rend.*, 1908, 147, 201—203. Compare *Abstr.*, 1898, i, 550).—The best bacterial culture for the oxidation of perseitol is that obtained by the spontaneous seeding of the juice of mountain ash berries. A 45% yield of *perseulose* is obtained. The new sugar has a sweet taste; the crystals resemble those of dextrose, but are better defined. The crystals are anhydrous, and have the composition C₇H₁₄O₇. They decompose on heating, and have no definite m. p.; on the Maquenne block they melt at about 110—115°. A freshly-prepared 10% aqueous solution has α_D^{25} not less than -90°; this falls rapidly, however, and after several hours becomes constant at -81°. The cupric reducing power of perseulose is less than that of dextrose, but considerably greater than that of sorbose.

The *osazone*, C₁₉H₂₄O₆N₄, crystallises from alcohol in silky needles, m. p. about 233°. W. O. W.

Products of the Reaction between Lactose and Calcium Hydroxide. HEINRICH KILIANI (*Ber.*, 1908, 41, 2650—2658).—Some of the products of the reaction between lactose and calcium hydroxide have been examined, but the investigation of the "residue" presented considerable difficulty (this vol., i, 128). The present communication deals with this difficulty. The reaction mixture is freed from the calcium salts of *isosaccharin* and *meta-saccharin*, and the resulting mother liquor, after removal of all the calcium by oxalic acid, is evaporated to a syrup, which is divided into four parts by extraction with (I) absolute ether (five times); (II) one part of absolute alcohol and two parts of ether, dried by calcium chloride (four times); (III) a mixture of equal parts of the preceding solvents (twice), and (IV)

absolute alcohol (twice). Each extraction, after removal of the solvents, is oxidised by nitric acid, D 1.4 (in the case of IV, D 1.2), whereby the most labile constituents are decomposed completely, whilst the saccharine substances are oxidised to di- and tri-basic acids, which can be more easily separated and characterised than the constituents of the original "residue." The author claims that the method must give some information as to the presence of compounds containing more or less than six atoms of carbon, and also as to the nature of the carbon chains in the products of the reaction between lactose and calcium hydroxide.

The paper contains a mass of detail unsuitable for abstraction. The main result is the detection of *l*-tartaric acid and of a tribasic acid, $C_6H_5O_8$ (probably identical with the α - γ -dihydroxypropane- α : α : γ -tricarboxylic acid obtained from *isosaccharin*), among the oxidation products of extracts II and III, and of a new dibasic acid, $C_6H_4O_8$, m. p. 159–160°, among the oxidation products of extract IV. Of this acid, which is feebly dextrorotatory, the *zinc*, *calcium*, *copper*, and *cadmium* salts are mentioned.

C. S.

Synthesis of Glucosides: Derivatives of Xylose. HUGH RYAN and GEORGE EBRILL (*Sci. Proc. Roy. Dubl. Soc.*, 1908, 11, 247–252. Compare Abstr., 1904, i, 223; Ryan, *Trans.*, 1899, 75, 1054; Ryan and Mills, *Trans.*, 1901, 79, 704).—A résumé is given of the work of various authors on the synthesis of acetylchloro-pentoses and -hexoses and of the corresponding glucosides. The preparation of a crystalline acetylchloroxylose and its conversion into a tetra-acetylxylose and into α -naphthyl- and carvacryl-xylosides are now described. Although the constitution of the acetylchloropentoses is uncertain, unless it is assumed that acetylchloroarabinose is the α -compound because Purdie and Rose obtained from it a product which they consider to be α -methylarabinoside (*Trans.*, 1906, 89, 1204), the phenol derivatives must be β -pentosides, since Fischer and Armstrong have shown that only β -hexosides are formed from both α - and β -acetylchlorohexoses in alkaline solution (Abstr., 1901, i, 671).

Acetylchloroxylose, $C_{11}H_{15}O_7Cl$, prepared by digesting xylose with acetyl chloride in a sealed tube in ice-water, separates from alcohol-chloroform in crystals, m. p. 101°, and on prolonged boiling with alcohol is converted into a non-reducing substance.

β -*Naphthylxyloside*, $C_{15}H_{16}O_5$, obtained by shaking acetylchloroxylose with α -naphthol and potassium hydroxide in alcoholic solution, crystallises from dilute alcohol in long needles, m. p. 192–193°, reduces Fehling's solution only after hydrolysis with dilute sulphuric acid, and is not hydrolysed by emulsin.

Carvacrylxyloside, $C_{15}H_{22}O_5$, prepared from carvacrol and acetylchloroxylose, crystallises from boiling water in long needles, m. p. 105°, and resembles β -*naphthylxyloside* in its behaviour towards Fehling's solution, but is more soluble in aqueous potassium hydroxide than in water.

When treated with silver acetate and glacial acetic acid, acetylchloroxylose is converted into tetra-acetylxylose, m. p. 119° (124°; Store, Abstr., 1894, i, 104).

G. Y.

Theoretical Investigations on the Charring of Wood. I. Dry Distillation of Cellulose. PETER KLASON, GUST. VON HEIDENSTAM, and EVERT NORLIN (*Arkiv. Kem. Min. Geol.*, 1908, 3, No. 1, 1—34).—The authors have investigated the products obtained by the dry distillation of cellulose derived from various sources. The results show that the charring of cellulose proceeds mainly according to the equation: $8C_6H_{10}O_5 = C_{80}H_{18}O_4$ (cellulose charcoal) + $23H_2O$ + $4CO_2$ + $2CO$ + $C_{12}H_{18}O_3$ (remaining products). The velocity of this reaction begins to become considerable at about 270° . At this temperature the dry distillation of cellulose is an exothermic process, the heat of the reaction being about 6% of the heat of combustion of cellulose. The gases evolved during the distillation have a heating value of about 3.5% of the heat of combustion of the cellulose, and include hydrogen and aromatic hydrocarbons. Methyl alcohol is not formed during the dry distillation of cellulose, and must hence be derived from the lignin of the wood. Acetic acid is formed during the dry distillation of cellulose, beech and birch cellulose yielding more of this acid than cotton, or fir or pine cellulose. T. H. P.

Chemical Composition of Pine-wood. I. PETER KLASON (*Arkiv. Kem. Min. Geol.*, 1908, 3, No. 5, 1—20).—From the liquid obtained by boiling pine-wood with calcium hydrogen sulphite, the author has prepared *barium lignosulphonate*, $C_{40}H_{44}O_{17}S_2Ba$, which in medium concentrations exhibits cryoscopic behaviour corresponding with a molecular weight of 4378—4675. It is assumed that lignin itself has the composition $C_{40}H_{44}O_{17}S_2Ba - BaH_2S_2O_6 = (C_{40}H_{42}H_{11})_n$. Both barium lignosulphonate and lignin give many colour reactions almost identical with those exhibited by coniferyl alcohol, and the latter, when treated with calcium hydrogen sulphite, yields a salt closely resembling calcium lignosulphonate. It is probable that lignin is formed by the condensation of coniferyl or hydroxyconiferyl alcohol. Both coniferyl alcohol and lignin are readily resinified by acids. Lignin contains 4OMe and 4OH per 40 carbon atoms, but lignosulphonic acid contains less than 4OMe. The author suggests the name "insoluble tannin" for lignin, owing to the great resemblance between the two substances; the side groups are probably in the same positions in lignin as in gallic acid. In lignosulphonic acid, part of the sulphurous acid is tightly and part loosely bound. T. H. P.

Chemical Composition of Pine-wood. II. PETER KLASON and OSCAR FAGERLIND (*Arkiv. Kem. Min. Geol.*, 1908, 3, No. 6, 1—10).—In order to ascertain whether lignin occurs in wood combined with sugars or other carbohydrates to form glucosidic compounds, the authors have investigated the matters extracted from pine-wood by boiling water, and by the latter and alcohol used alternately.

It is found that boiling water dissolves about 12% of the dry matter of the wood, about 10% consisting of wood-gum and 2% of substances resembling true lignin. The wood-gum obtained is only sparingly soluble in alkali solution, and contains 25% of xylose, 6% of mannose, and traces of galactose, the remainder apparently consisting of unknown sugars. The other substances, resembling lignin, extracted by water

consist partly of coniferyl alcohol and of a substance which is apparently a dimeric form of hydroxyconiferyl alcohol or similarly constituted compound. Lignin does not occur in wood in combination with carbohydrates.

T. H. P.

Constitution of Certain Cyanogen Compounds. F. CARLO PALAZZO and GIUSEPPE SCELSI (*Gazzetta*, 1908, **38**, i, 659—681. Compare Palazzo and Carapelle, *Abstr.*, 1907, i, 195).—The authors have applied the action of diazomethane to thiocyanic acid, cyanamide, and cyanuric and thiocyanuric acids with the object of determining the structure of these compounds. In each case, only one of the two possible isomeric esters was obtained, the yield being quantitative.

Cyanuric acid and diazomethane yield only trimethyl isocyanurate, a result which confirms Hantzsch's conclusion (*Abstr.*, 1906, i, 146) that solid cyanuric acid is a complete pseudo-acid containing three $\text{CO}\cdot\text{NH}$ groups, and is, hence, tricarbimide.

On the other hand, thiocyanic acid yields methyl thiocyanate free from any trace of compound capable of combining with ammonia, so that the acid has the normal structure $\text{N}\equiv\text{C}\cdot\text{SH}$.

Thiocyanuric acid and diazomethane give a mixed trimethyl derivative, in which part of the methyl is combined with sulphur and part with nitrogen. This acid is, hence, a partial pseudo-acid, since it forms a completely normal trisodium salt, whilst in the free state a part (one-third or two-thirds) of the HCNS groups is not directly halogenic or salt-forming.

With cyanamide, diazomethane or diazoethane yields a trisubstituted isoumelamine, which can only be formed by the polymerisation of the compound $\text{NH}\cdot\text{C}\cdot\text{NMe}$ (or Et), so that cyanamide must be regarded as carbodi-imide, $\text{NH}\cdot\text{C}\cdot\text{NH}$.

T. H. P.

Tautomerism of the Cyanogen Compounds. H. GUILLEMAUD (*Ann. Chim. Phys.*, 1908, [viii], **14**, 311—432).—The paper commences with an historical résumé of the controversy concerning the isomerism of the nitriles and the carbylamines. This is followed by a detailed description of the analytical methods previously devised (*Abstr.*, 1907, i, 141) for the estimation of the nitriles and the carbylamines when alone, when mixed together, and when present in the mixture resulting from the action of an alkylating agent on a metallic cyanide. A complete account of experiments on the polymerisation and isomeric change of the carbylamines, the results of which have been previously published (*Abstr.*, 1907, i, 197), is given. When the mixture of phenylcarbylamine, aniline, and diphenylformamidine resulting from the action of alcoholic potash on a solution of aniline in chloroform is treated with silver cyanide, and the phenyl argenticyanide produced treated with potassium cyanide, after washing with ether, the product consists, not of phenylcarbylamine, but of a reddish-brown substance, crystallising in long, silky needles, m. p. 113° , which, when heated above its melting point, regenerates the carbylamine.

The author discusses the stereochemistry of nitrogen in the nitriles and carbylamines, and points out that the nitrogen only becomes

quinquevalent after the saturation of the carbon. Thus when ethyl-carbylamino dibromide is treated with hydrogen sulphide in carbon disulphide solution, ethylthiocarbimide and ethyl dibromocarbimide are formed: $\text{NEt:CBBr}_2 + \text{H}_2\text{S} = \text{NEt:CS} + 2\text{HBr}$; $\text{NEt:CBBr}_2 + \text{HBr} = \text{NHEtBr:CBBr}_2$, whilst hydrogen chloride and ethyl iodide give analogous compounds. Ethyl alcohol reacts very violently with ethylcarbylamine dibromide, giving hydrogen and ethyl bromides and Gal's ethylcarbimide hydrobromide, NHBrEt:CO .

The third part of the paper is devoted to a detailed account of the experiments (Abstr., 1907, i, 300) on the action of alkylating agents (alkyl iodides and alkali alkyl sulphates) on many simple and complex metallic cyanides.

Finally, the author has determined the heats of combustion of some carbylamines and alkyl argenticyanides. The carbylamines, in order to secure complete combustion, were weighed in small glass vessels, covered with a weighed film of collodion, and, to the same end, a small quantity of water was introduced into the calorimetric bomb to avoid the deposition of carbon beneath the glass vessel. The following are the results obtained:

	Molecular heat of combustion.	Molecular heat of formation.
Methylcarbylamine	+ 320.1 Cal.	- 28.0 Cal.
Ethylcarbylamine	480.1 "	- 24.7 "
n-Propylcarbylamine	638.9 "	- 20.2 "
iso-Butylcarbylamine	795.0 "	- 13.0 "
iso-Amylcarbylamine	948.15 "	2.85 "
Allylcarbylamine	608.8 "	- 59.1 "
Benzylcarbylamine	1045.35 "	- 49.45 "

By extrapolation from these figures, the values + 159.1 Cal. and - 31.0 Cal. are obtained for the heats of combustion and formation of the lowest member of the homologous series, namely, carbylamine itself, HNC , whilst the values + 136 Cal. and - 7.8 Cal. are similarly deduced for hydrogen cyanide, HCN , from the numbers observed by Berthelot for acetonitrile and propionitrile. Since the values experimentally observed by Berthelot for hydrocyanic acid are + 159.3 Cal. and - 30.5 Cal. respectively, the thermochemical evidence indicates that this acid is a carbylamine and not a nitrile.

Propylcarbylamine, $\text{NPr}^{\text{a}}\text{:C}$, prepared by the action of propyl iodide on silver cyanide and subsequent decomposition of the propyl argenticyanide with potassium cyanide, is a liquid, b. p. 99.5°. *iso-Butylcarbylamine*, prepared similarly, has b. p. 110—111°.

The alkyl argenticyanides are prepared either by melting together molecular quantities of potassium argenticyanide and the alkali alkyl sulphate, or by the addition of silver cyanide to the carbylamino dissolved in ethyl alcohol. They are well-crystallised, colourless compounds, which decompose at the ordinary temperature, evolving the carbylamine, and are decomposed by boiling aqueous alkali hydroxides, by strong acids, and by halogens, but not by hydrogen sulphide. Owing to their instability, their heats of combustion could only be determined accurately in the presence of excess of the carbylamines.

The following are the results obtained :

	Molecular heat of combustion.	Molecular heat of formation.	Heat of combination (AgNC + RNC)
Methyl argenticyanide ...	+ 440.4 Cal.	- 54.0 Cal.	+ 7.0 Cal.
Ethyl argenticyanide.....	600.5 "	- 50.8 "	+ 6.9 "
n-Propyl argenticyanide..	759.5 "	- 46.5 "	+ 6.7 "
isoButyl argenticyanide...	916.4 "	- 40.1 "	+ 5.9 "
isoAmyl argenticyanide...	1071.0 "	- 31.4 "	+ 4.5 "

These figures show that the argenticyanides as well as the carbylamines are strongly endothermic compounds, whilst the combination of silver cyanide with the carbylamine is exothermic. The gradual decrease of the values in the last column explains the increase in the tension of dissociation with increasing carbon-content.

Ethyl cuprocyanide, large, colourless prisms, *propyl cuprocyanide*, rhombic tablets, and *isobutyl cuprocyanide*, rhombic prisms of the general formula CuN:C:C:NR , have similar properties to the silver compounds, and are prepared in a similar manner.

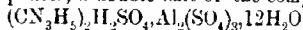
The conclusions drawn are that hydrocyanic acid and its metallic salts must be formulated as isocyanides, giving carbylamines with alkylating agents, that the organometallic compounds of the carbylamines decompose into nitriles and carbylamines, the proportion of each depending on the temperature and nature of the alkyl group present, and that the cyanides do not exhibit any phenomena of tautomerism.

E. H.

Preparation of Halogen-substituted Acetonitriles. WILHELM STEINKOFF (*Ber.*, 1908, 41, 2540—2542. Compare Braun, this vol., i, 627, 675).—Chloroacetonitrile is readily prepared in a 70% yield by distillation of a mixture of chloroacetamide and phosphoric oxide from a glass flask (compare Scholl, Abstr., 1897, i, 9) under 200 mm. and, finally, under 11 mm. pressure (Abstr., 1907, i, 490). Bromoacetonitrile is obtained in the same manner from bromoacetamide in a 60% yield (Abstr., 1905, i, 756). Trichloro- and tribromo-acetonitriles are best prepared by distillation of the amides with phosphoric oxide under the ordinary pressure. Iodoacetonitrile is obtained in good yields by the action of potassium iodide on crude chloroacetonitrile.

G. Y.

Double Sulphate of Guanidine and Aluminium. F. FERRABOSCHI (*Proc. Camb. Phil. Soc.*, 1908, 14, 471—474).—From a solution containing approximately equivalent quantities of guanidines and aluminium sulphates, a double salt of the composition



crystallises in large, well-developed, hexagonal prisms terminated by basal planes. The crystals exhibit a perfect basal cleavage, and probably belong to the scalenohedral class of the rhombohedral system; D^{110} 1.806.

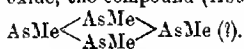
H. M. D.

Reactions of the Arsines. WILLIAM M. DEHN (*Amer. Chem. J.*, 1908, 40, 88—127. Compare Abstr., 1905, i, 184; 1906, i, 150, 341).—The reactions of arsenic compounds cannot always be explained on the basis either of ionic or of kineto-molecular mechanics. Most of

the arsenic reactions are non-electrolytic, and between the initial compounds and the most easily separable end-product other compounds, usually crystalline, are formed and can often be separated. The present paper describes a systematic study of the reactions of the arsines, evidence being obtained showing that intermediate products are often formed and that arsenic compounds react largely by initial coalescence with the reagent. In most of the reducing actions effected by the arsines, there is evidence of an initial amalgamation of the oxidising agent and the arsine. Also, in the interaction of sodium arsenite with alkyl iodides, according to the equation $\text{Na}_3\text{AsO}_3 + \text{RI} = \text{Na}_2\text{RAsO}_3 + \text{NaI}$, the additive compound $\text{AsIR}(\text{ONa})_2$ is formed as an intermediate product.

In the electrolytic reduction of cacodyl chloride to dimethylarsine, cacodyl is first formed, the successive reactions being $2\text{AsMe}_2\text{Cl} + 2\text{H} = \text{AsMe}_2\cdot\text{AsMe}_2 + 2\text{HCl}$ and $\text{AsMe}_2\cdot\text{AsMe}_2 + 2\text{H} = 2\text{AsHMe}_2$.

[With ELRICK WILLIAMS.]—A large number of reactions of methylarsine were studied, and equations are given for the changes taking place. The reactions represented by the equations: $\text{AsMeH}_2 + \text{HI} \rightleftharpoons \text{AsMeH}_2\text{I} \rightarrow \text{AsMeHI} + \text{H}_2$ and $\text{AsMeHI} + \text{HI} \rightleftharpoons \text{AsMeH}_2\text{I}_2 \rightarrow \text{AsMeI}_3 + \text{H}_2$ are slow or readily reversible. Methylarsine gives (1) with propyl iodide, AsH_2MePrI , the reaction being reversible; (2) with silver nitrate, a mixture of silver methylarsinate and silver; (3) with methylarsine oxide, the compound $(\text{AsMe})_4$ or

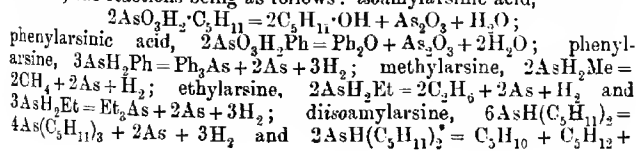


Ethylarsine reacts with (1) iodine, $\text{AsH}_2\text{Et} + \text{I}_2 = \text{AsI}_2\text{Et} + \text{H}_2$; (2) bromine, $\text{AsH}_2\text{Et} + \text{Br}_2 = \text{AsBr}_2\text{Et} + \text{H}_2$, intermediate products being formed; (3) sulphur, $\text{AsH}_2\text{Et} + \text{S}_2 = \text{AsEtS} + \text{H}_2\text{S}$; (4) mercuric chloride, $\text{AsH}_2\text{Et} + 2\text{HgCl}_2 = \text{AsCl}_2\text{Et} + 2\text{Hg} + 2\text{HCl}$; (5) mercuric iodide, $\text{AsH}_2\text{Et} + 2\text{HgI}_2 = \text{AsI}_2\text{Et} + 2\text{HgI} + \text{H}_2$; (6) stannic chloride, $\text{AsH}_2\text{Et} + 2\text{SnCl}_4 = \text{AsCl}_2\text{Et} + 2\text{SnCl}_2 + 2\text{HCl}$; (7) arsenic trichloride, $8\text{AsH}_2\text{Et} + 8\text{AsCl}_3 = (\text{AsEt})_4 + 4\text{AsCl}_2\text{Et} + 16\text{HCl} + 8\text{As}$; (8) propyl iodide, giving *ethyltripropylarsonium iodide*, AsEtPr_3I , m. p. 237° (decomp.); (9) isopropyl iodide, giving *ethyltriisopropylarsonium iodide*, which decomposes at its melting point according to the equations: $\text{AsEtPr}_3\text{I} = \text{AsPr}_3 + \text{EtI}$ and $2\text{AsEtPr}_3\text{I} = \text{AsPr}_3\text{I}_2 + \text{C}_3\text{H}_{10} + \text{AsPr}_3$.

Benzylarsine, $\text{AsH}_2\cdot\text{CH}_2\text{Ph}$, prepared by reducing benzylarsinic acid by means of amalgamated zinc dust and hydrochloric acid, is a faintly yellow liquid, b. p. $140^\circ/262$ mm., oxidises in the air to benzylarsinic acid, and forms a *platinichloride*, $\text{C}_6\text{H}_7\text{AsH}_2\text{PtCl}_4$.

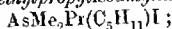
Tripropylarsine, AsPr_3 , prepared by the interaction of propyl chloride, arsenic trichloride, and sodium, has b. p. $167^\circ/90$ mm. and $158^\circ/73$ mm.

The decomposition of various arsenic derivatives by heat has been studied, the reactions being as follows: *isoamylarsinic acid*,



$C_{10}H_{22} + 2As$; diphenylarsine, $6AsHPh_2 = 4AsPh_3 + 2As + 3H_2$ and $2AsPh_3 = 3C_{12}H_{10} + 2As$; tripropylarsine, $4AsPr^a_3 = (AsPr^a)_4 + 4C_3H_4$; triethylarsine, $4AsEt_3 = (AsEt)_4 + 4C_4H_{10}$; benzylarsine, $4AsH_2 \cdot CH_2Ph \rightarrow (As \cdot CH_2Ph)_4 + 4H_2$; cacodyl, $4AsMe_2 \cdot AsMe_2 \rightarrow 4AsMe_3 + (AsMe)_4$.

[With BURTON B. WILLCOX.]—Dimethylarsine gives the following reactions: (1) With phenylarsino dichloride it yields dimethylarsine-phenylarsine dichloride, $AsCl_2Ph \cdot AsHMe_2$, which decomposes rapidly in the air; (2) with diisoamylarsine chloride, dimethyldiisoamyl-cacodyl, $AsMe_2 \cdot As(C_5H_{11})_2$, is obtained; (3) with propyl iodide it yields *dimethylpropylarsonium iodide*, $AsHMe_2Pr^aI$, which, with *isoamyl iodide*, gives *dimethylpropylisoamylarsonium iodide*,



(4) with acetyl iodide it forms $AsHMe_2AcI$ which decomposes, giving $AsMe_2I + CH_3 \cdot CHO$; (5) with ethyl chlorocarbonate, dimethylarsine reacts thus: $AsHMe_2 + Cl \cdot CO_2Et \rightarrow AsMe_2Cl + H \cdot CO_2Et$; (6) with sulphur dichloride, $2AsHMe_2 + SCl_2 \rightarrow 2AsMe_2Cl + S$; (7) with arsenic trioxide, $2AsHMe_2 + As_2O_3 = (AsMe)_4 + H_2O + O_2$; (8) with arsenic trichloride, $4AsHMe_2 + 2AsCl_3 = (AsMe)_4 + 2AsMe_2Cl + 4HCl$.

Diisoamylarsine and propyl iodide yield dipropyldiisoamylarsonium iodide, $AsPr^a_2(C_5H_{11})_2I$, and cacodyl and propyl iodide, *dimethyl-dipropylarsonium iodide*, $AsMe_2Pr_2I$, which, with mercuric chloride, gives a white precipitate, $AsMe_2Pr_2I, HgCl_2$. T. II. P.

cycloHexadienes. II. NICOLAI D. ZELINSKY and A. GORSKY (*Ber.*, 1908, **41**, 2630—2634. Compare this vol., i, 619).—A pronounced exaltation of the molecular refraction is not shown by the following hydrocarbons containing conjugate double linkings. 1-Methyl-2'-*cyclohexene* yields a *dibromide*, b. p. 100—102°/12 mm., from which by means of quinoline, 1-methyl- $\Delta^{2:4}$ -*cyclohexadiene* is obtained, which has b. p. 110°(corr.)/741 mm., D_4^{20} 0.8292, n_D^{20} 1.4710, and gives a blood-red coloration with alcoholic sulphuric acid and a bluish-violet with nitric acid (D 1.40). 1:3-Dimethylcyclohexene yields a *dibromide*, b. p. 130—135°/35 mm., which by distillation with quinoline yields 1:3-dimethyl- $\Delta^{2:4}$ -*cyclohexadiene*, b. p. 129—130°/745 mm., D_4^{20} 0.8225, n_D^{20} 1.4675, $[\alpha]_D^{20}$ 27.38°. 1:4-Dimethylcyclohexan-4-ol and aqueous oxalic acid yield 1:4-dimethyl- Δ^3 -*cyclohexene*, b. p. 128.5°(corr.), D_4^{20} 0.8005, n_D^{20} 1.4457, the *dibromide* of which, by repeated distillation with quinoline, yields 1:4-dimethyl- $\Delta^{2:4}$ -*cyclohexadiene*, b. p. 132.5—133.5°(corr.)/740 mm., D_4^{20} 0.8223, n_D^{20} 1.4675. 1:2-Dimethylcyclohexan-2-ol and aqueous oxalic acid yield 1:2-dimethyl-*cyclohexene*, b. p. 135.5—136.5°(corr.), D_4^{20} 0.8226, n_D^{20} 1.4580, the derivatives of which will be considered later. C. S.

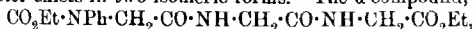
Mechanism of the Autoracemisation of Optically Active Ammonium Salts and the State of Quaternary Ammonium Salts in Solution. EDGAR WEDEKIND and F. PASCHKE (*Ber.*, 1908, **41**, 2659—2665).—von Halban's measurements with inactive ammonium salts (*Abstr.*, 1907, ii, 246) do not decide whether the racemisation of

the active salts is due solely to decomposition into a tertiary base and an alkyl haloid, or is conditioned partly by intramolecular changes. That the latter alternative may be of influence is shown by the fact that active methylallyltetrahydroquinolinium iodide in methyl alcohol racemises with extraordinary velocity, although theoretically it should be stable in this solvent. The authors have therefore examined phenylbenzylmethylallyl-(or propyl)ammonium bromide and iodide polarimetrically, cryoscopically, by a slightly modified form of von Halban's titrimetric method, and by direct weighing of the undecomposed salt precipitated by ether. In every case the velocity constant of the decomposition agrees well with that of the racemisation. Ammonium salts, therefore, in suitable solvents (see later) decompose into a tertiary base and an alkyl haloid, a phenomenon which in the case of active salts is accompanied by an equally rapid diminution of the rotation. The deduction that active and inactive salts of the same base must decompose at the same rate has been verified. Moreover, the point of equilibrium of the system $RR'R''N \rightleftharpoons R'R''N + RX$ must be the same for the active and the inactive modification of the same salt (compare von Halban, *loc. cit.*). This point differs greatly in bromides and iodides; in the former it corresponds with 40—50% of unchanged salt, and in the latter to 6%, at 25°. The preceding equation does not represent truly the condition of affairs in the solution, since the partition-coefficient in chloroform and cryoscopic measurements in bromoform indicate that ammonium salts are present in the solution in the bimolecular state.

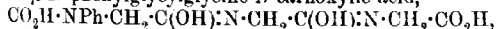
The nature of the solvent is of importance. Water and alcohol at 45° do not decompose quaternary ammonium salts appreciably, but in solvents with a small dielectric constant, such as tetrachloroethane, benzene, carbon disulphide, or ethylene tetrabromide (with the addition of alcohol to facilitate solution), the decomposition of an active ammonium salt can be followed with the polarimeter.

C. S.

Isomerism of Carbethoxydiglycylglycine Ester and the Stability of *N*-Carboxylic Acids. HERMANN LEUCHS and FREDERICK B. LA FORGE (*Ber.*, 1908, 41, 2586—2596. Compare Leuchs and Manasse, *Abstr.*, 1907, i, 770).—Carbethoxy-*N*-phenylglycylglycylglycine ester exists in two isomeric forms. The α compound,

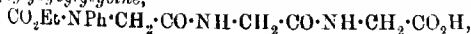


is obtained synthetically by the action of glycylglycine ester on carbethoxy-*N*-phenylglycyl chloride. When suitably hydrolysed, it yields the β -*N*-phenylglycylglycine-*N*-carboxylic acid,

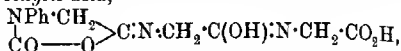


the silver salt of which reacts with ethyl iodide, yielding the isomeric β ester,

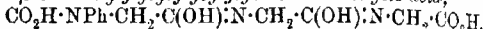
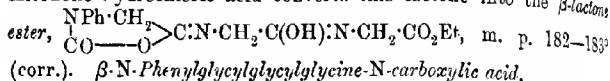
α -Carbethoxy-*N*-phenylglycylglycylglycine ester crystallises from benzene in small, colourless needles, m. p. 135—136°. When hydrolysed with sodium hydroxide (1 mol.), it yields α -carbethoxy-*N*-phenylglycylglycylglycine,



which can also be synthesised from glycylglycine and carbethoxy-phenylglycyl chloride. It crystallises from ethyl acetate in needles, m. p. 145—146° after sintering at 141°, or from water in hydrated needles. When boiled with sodium hydroxide (2 mols.) and then acidified, the acid ester yields the lactone of β -phenylglycylglycylglycine-*N*-carboxylic acid,



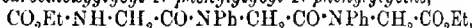
which crystallises from water and has m. p. 212—213° (corr.). Alcoholic hydrochloric acid converts this lactone into the β -lactone



is obtained by carefully hydrolysing the α -ester, and when boiled with water or dilute hydrochloric acid readily yields the lactone acid, m. p. 212—213°. The β -ester, obtained from the silver salt of the β -acid, is a thick oil, and when boiled with alcoholic hydrochloric acid yields the lactone ester, m. p. 182—183°.

Carbethoxyglycyl-N-phenylglycine, $\text{C}_{13}\text{H}_{16}\text{O}_5\text{N}_2$, obtained by hydrolysing the corresponding ester (Abstr., 1907, i, 770), crystallises from benzene in colourless plates, m. p. 133—134°. The corresponding chloride reacts with ethyl glycine, yielding *ethyl carbethoxyglycyl-N-phenylglycylglycine*, $\text{CO}_2\text{Et}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NPh}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, which crystallises from benzene or hot water in large prisms, m. p. 144—145° (corr.). When the ester is boiled with three equivalents of barium hydroxide, only some 30% of the theoretical amount of carbon dioxide is removed. The elimination of carbon dioxide is probably due to the fact that part of the ester is not transformed into the β -isomeride, but is directly hydrolysed, and the resulting α -acid immediately loses carbon dioxide.

Ethyl carbethoxyglycyl-N-phenylglycyl-N-phenylglycine,



obtained by condensing ethyl phenylglycine with carbethoxyglycyl-*N*-phenylglycyl chloride, has not been obtained in a crystalline form; the corresponding acid, $\text{C}_{21}\text{H}_{28}\text{O}_6\text{N}_4$, crystallises from ethyl acetate in nodules and contains $1\text{H}_2\text{O}$. When rapidly heated, it melts and decomposes at 128—130°. When boiled with excess of sodium hydroxide, the elimination of carbon dioxide is almost theoretical.

Ethyl carbethoxyglycylsarcosine,



crystallises from ether in long prisms, m. p. 54—55°, and, when hydrolysed with sodium hydroxide, loses an appreciable amount of carbon dioxide.

The results support the view that it is the α -(lactam)compounds which yield carbon dioxide, and when substituents are attached to the nitrogen atom so that molecular rearrangement into the isomeric β -(lactim)compound cannot take place, carbon dioxide is always eliminated during hydrolysis.

J. J. S.

salts \

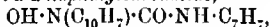
***N*-α-Naphthylhydroxylamine.** II. JOHANNES SCHEIBER [and, in part, ERNST BECKMANN] (*J. pr. Chem.*, 1908, [ii], 78, 74—80. Compare Abstr., 1904, i, 867).—Two of the most characteristic reactions of the β-substituted hydroxylamines are the formation of *N*-aldoxime ethers, $\text{CHR} \begin{smallmatrix} \text{NR} \\ \diagup \\ \text{O} \end{smallmatrix}$, by condensation with aldehydes, and of disubstituted hydroxycarbamides, $\text{OH} \cdot \text{NR} \cdot \text{CO} \cdot \text{NHPh}$, by addition of phenylcarbimide (Beckmann, Abstr., 1898, i, 22). Although containing the elements of a mol. of water more than other *N*-arylhydroxylamines, *N*-α-naphthylhydroxylamine is found also to undergo these typical reactions.

The following *N*-α-naphthylaldoximes, $\text{CHR} \begin{smallmatrix} \text{N} \cdot \text{C}_{10}\text{H}_7 \\ \diagup \\ \text{O} \end{smallmatrix}$, are described:

R = Ph: yellow crystals, m. p. 106.5°, decomposes, becoming red on exposure to light. R = C₆H₄·OMe(*p*): yellow crystals, m. p. 159°. R = C₆H₄·OH(*o*): yellow crystals, m. p. 153°. R = C₆H₄·NO₂(*m*): m. p. 147°.

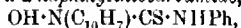
a-Hydroxy-*b*-phenyl-α-naphthylcarbamide, $\text{OH} \cdot \text{N}(\text{C}_{10}\text{H}_7) \cdot \text{CO} \cdot \text{NHPh}$, formed from *N*-α-naphthylhydroxylamine and phenylcarbimide, is obtained in white crystals, m. p. 126°, and gives an intense blue coloration with ferric chloride in alcoholic solution.

a-Hydroxy-*b*-*p*-tolyl-α-naphthylcarbamide,



formed from *N*-α-naphthylhydroxylamine and *p*-tolylcarbimide, separates from alcohol in crystals, m. p. 147°, and gives a blue coloration with ferric chloride.

a-Hydroxy-*b*-phenyl-α-naphthylthiocarbamide,



prepared from *N*-α-naphthylhydroxylamine and phenylthiocarbimide, forms nodular crystals, m. p. 119°, and gives a black solution with alcoholic ferric chloride. G. Y.

***N*-α-Naphthylhydroxylamines.** III. JOHANNES SCHEIBER and PAUL BRANDT (*J. pr. Chem.*, 1908, [ii], 78, 80—92. Compare preceding abstract).—The *N*-aldoxime ethers derived from *N*-α-naphthylhydroxylamine behave towards mineral acids and alkalis in the same manner as other *N*-arylaldoximes, yielding the aldehyde and transformation products of the *N*-α-naphthylhydroxylamine, chiefly azoxy-naphthalene. On the other hand, the isolation of an additive compound of *N*-α-naphthylhydroxylamine and phenylcarbimide has not been achieved. *N*-Aldoxime ethers, in general, are transformed by acid chlorides or anhydrides into the isomeric amides. The transformation takes place readily and at low temperatures with benzoyl or acetyl chloride, benzoylated and acetylated amides being formed with an excess of the acid chloride at high temperatures, but only at high temperatures with benzoic anhydride, when the benzoylated amide is formed. As, however, Wortmann (*Diss.*, Leipzig, 1903) found that the action of benzoic anhydride on *N*-α-naphthylbenzaldoxime leads to the formation of *N*-benzoyl-1-amino-β-naphthol, it was of interest to study the mechanism of this reaction.

It is found now that *N*-benzoyl-1-amino- β -naphthol is formed by the action of benzoic anhydride, not only on *N*- α -naphthylbenzaldoxime, but also on *N*- α -naphthylanisaldoxime or on *N*- α -naphthylhydroxylamine, in the last case being accompanied by small amounts of dibenzoyl-1-amino- β -naphthol, which is formed also by the action of an excess of benzoic anhydride on *N*- α -naphthylanisaldoxime. On the other hand, the action of benzoic anhydride on *N*-anisoyl-1-amino- β -naphthol leads to the formation of *O*-benzoyl-*N*-anisoyl-1-amino- β -naphthol, together with small amounts of *N*-benzoyl- and unchanged *N*-anisoyl-1-amino- β -naphthol. It is argued that the action of benzoic anhydride on *N*- α -naphthylaldoximes must, therefore, consist in the first place of a fission of the aldoxime with formation of *N*- α -naphthylhydroxylamine, and not of an addition of the anhydride to the *N*-aldoxime ether.

When gently heated with acetic anhydride, *N*- α -naphthylanisaldoxime yields *N*-acetyl-1-amino- β -naphthol (Michel and Grandmougin, *Abstr.*, 1893, i, 171).

[For the benzoyl and anisoyl derivatives of 1-amino- β -naphthol, see abstract below.] G. Y.

Transformation of Benzhydroxamic Acid into Anilides. GIACOMO PONZIO and R. GIOVETTI (*Gazzetta*, 1908, 38, i, 655-657).—When benzhydroxamic acid is treated in alkaline solution with an aryl diazo-chloride, it is converted into its corresponding unstable diazo-salt, and this, when heated with alcohol, is converted into an anilide of benzhydroxamic acid.

Thus, with diazobenzene chloride, benzanilide is obtained; with *o*-diazotoluene chloride, benzo-*o*-toluidide; with *p*-diazotoluene chloride, benzo-*p*-toluidide; with *p*-diazobenzene chloride, benzo-*p*-anisidide, and with *as-m*-diazoxylene chloride, benzo-*m*-xylylide. T. H. P.

***syn*- and *anti*-Stereoisomerism of Nitrogen Compounds.** JULIUS STIEGLITZ (*Amer. Chem. J.*, 1908, 40, 36-46).—The author gives a résumé of the various pairs of stereoisomeric chloroimino-esters prepared by him in conjunction with Earle (*Abstr.*, 1904, i, 39) and others, and discusses them in relation to Hantzsch and Werner's hypothesis of *syn*- and *anti*-stereoisomerism. T. H. P.

Derivatives of 1-Amino- β -naphthol. JOHANNES SCHEIBER and PAUL BRANDT (*J. pr. Chem.*, 1908, [ii], 78, 92-95. Compare this vol., i, 725).—*N*-Benzoyl-1-amino- β -naphthol, m. p. 248° (245°: Böttcher, *Abstr.*, 1883, 1113), is prepared by heating 1-amino- β -naphthol hydrochloride and sodium acetate with benzoic anhydride in glacial acetic acid solution.

Dianisoyl-1-amino- β -naphthol, $C_{26}H_{21}O_3N$, formed by shaking 1-amino- β -naphthol with anisoyl chloride and aqueous sodium hydroxide, separates from methyl alcohol in crystals, m. p. 215°, and, when treated successively with alcoholic sodium ethoxide and hydrochloric acid, yields *N*-anisoyl-1-amino- β -naphthol, $C_{18}H_{15}O_3N$, crystallising in golden leaflets, m. p. 241-243°.

N-Benzoyl-O-anisoyl-1-amino-β-naphthol, $C_{25}H_{19}O_4N$, m. p. 181° , is obtained by the action of anisoyl chloride and sodium hydroxide on *N*-benzoyl-1-amino-β-naphthol, and yields *N*-benzoyl-1-amino-β-naphthol when treated with alcoholic sodium hydroxide.

O-Benzoyl-N-anisoyl-1-amino-β-naphthol, m. p. 189° , is formed by benzoylation of *N*-anisoyl-1-amino-β-naphthol, and yields this when hydrolysed with alcoholic sodium hydroxide.

G. Y.

Oxidation of Eugenol by the Oxidising Ferment of Mushrooms. Formation of Dehydrodieugenol. H. COUSIN and HENRI HÉRISSEY (*Compt. rend.*, 1908, 146, 1413—1415. Compare this vol., i, 84).—Oxidation with ferric chloride or with air in presence of the oxydase from *Russula delica*, forms in very dilute eugenol solutions a precipitate of *dehydrodieugenol*, $C_{20}H_{22}O_4$, leaflets, m. p. 105 – 106° , giving a blue coloration with ferric chloride, and still having a double linking. *Diacyldehydrodieugenol*, $C_{24}H_{26}O_6$, melts at 91 – 92° , and *dibenzoyldehydrodieugenol*, $C_{34}H_{30}O_8$, melts at 170 – 171° .

G. B.

cycloHexanylethyl Alcohol and cycloPentanylcarbinol. NICOLAI D. ZELINSKY (*Ber.*, 1908, 41, 2628—2629).—The reaction between magnesium *cyclohexanyl* iodide and trioxymethylene in dry ether leads to the formation of *cyclohexanylethyl alcohol*, $C_6H_{11}\cdot CH_2\cdot CH_2\cdot OH$, b. p. 206 – $207^\circ/745$ mm. and 97 – $100^\circ/12$ mm., D_4^{20} 0.9153, n_D^{20} 1.4647. *cycloPentanylcarbinol*, $C_5H_9\cdot CH_2\cdot OH$, obtained from magnesium *cyclopentanyl* chloride and trioxymethylene, has b. p. 162.5 – 163.5° (corr.), D_4^{20} 0.9260, n_D^{20} 1.4555, forms a *phenylcarbamate*, m. p. 110° (corr.), and is oxidised to the corresponding *aldehyde* by 10% chromic acid in dilute acetic acid.

C. S.

New Synthesis of Derivatives of Anthracene. HANS VON LIEBIG (*J. pr. Chem.*, 1908, [ii], 78, 95—96).—When fused with mandelic acid at 200 – 300° , the three dihydroxybenzenes form the corresponding dihydroxydiphenylmethanecarboxylic acids, but catechol and quinol yield also crystalline dyes, which in their behaviour resemble the dihydroxyanthraquinones, but are meso-ethers and are insoluble in aqueous sodium carbonate. These dyes are considered to

have the constitution $C_6H_2(OH)_2 \begin{array}{c} \diagup \quad \diagdown \\ \text{C} \quad \text{O} \quad \text{C} \\ | \quad | \quad | \\ \text{C}_6H_4 \quad \text{C}_6H_4 \quad \text{C} \\ \diagdown \quad \diagup \\ \text{C} \quad \text{O} \quad \text{C} \end{array} \begin{array}{c} \diagdown \quad \diagup \\ \text{C} \quad \text{O} \quad \text{C} \\ | \quad | \quad | \\ \text{C}_6H_4 \quad \text{C}_6H_4 \quad \text{C} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{O} \quad \text{C} \end{array} C_6H_2(OH)_2$.

2:2':3:3'-Tetrahydroxydianthranol meso-ether, $C_{28}H_{16}O_8$, prepared from catechol and mandelic acid, crystallises in glistening, bronze-coloured leaflets, m. p. 264° , and dissolves in benzene or alcohol to a red, or in aqueous alkalis to a blue, solution.

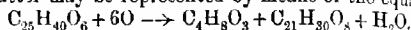
1:1':4:4'-Tetrahydroxydianthranol meso-ether, formed from quinol and mandelic acid, crystallises in violet-red needles, m. p. 298° , and dissolves in benzene or alcohol to a red, or in aqueous alkalis to a violet, solution.

2:5-Dihydroxydiphenylmethanecarboxylic acid lactone, m. p. 157° (153 – 154° ; Bistrzycki and Flatau, *Abstr.*, 1895, i, 419), obtained

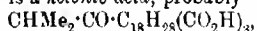
from quinol and mandelic acid, 2:4-dihydroxydiphenylmethanecarboxylic acid lactone, m. p. 183°, from resorcinol and mandelic acid, and 2-hydroxy-4-methyldiphenylmethanecarboxylic acid lactone, m. p. 124°, from *m*-cresol and mandelic acid, give colorations with concentrated sulphuric acid.

G. Y.

Cholesterol. XI. ADOLF WINDAUS (*Ber.*, 1908, 41, 2558—2568).—When the tribasic acid, $C_{25}H_{40}O_6$ (this vol., i, 265), is heated for eight hours at 75° with a mixture of equal volumes of fuming nitric and glacial acetic acids, the products are a trinitro-acid, $C_{25}H_{37}O_{12}N_3$, a tetrabasic acid, $C_{21}H_{30}O_8$, and α -hydroxyisobutyric acid; the formation of the two latter may be represented by means of the equation



The trinitro-acid is precipitated on the addition of water, and may be purified by washing with ethyl acetate and subsequent recrystallisation from glacial acetic acid. It forms colourless, glistening, rhombic plates, m. p. 234—235° (decomp.). It is a tribasic acid, and yields a *monorubidium* salt, $C_{25}H_{37}O_{12}N_3Rb$, which crystallises readily from 50% alcohol, and also an *acid potassium* salt, $C_{25}H_{34}O_{12}N_3K_3 \cdot C_{25}H_{37}O_{12}N_3$. When reduced with zinc dust and acetic acid, the trinitro-acid yields acetone and a nitrile, $C_{22}H_{31}O_6N$. The formation of acetone is in harmony with the view that the nitro acid contains the grouping $NO_2 \cdot CMe_2 \cdot C(NO_2)_2$, and hence the original tribasic acid may be represented by the formula $CHMe_2 \cdot CH_2 \cdot C_{18}H_{25}(CO_2H)_3$. Among the products of reduction is a *ketonic acid*, probably



which yields a crystalline *oxime*, $C_{25}H_{39}O_7N$, m. p. 230—231° (decomp.). The *nitrile*, $C_{22}H_{31}O_6N$, crystallises from dilute acetic acid in needles and prisms, m. p. 137—138° after sintering at 127°. It is a tribasic acid, and, when boiled with potassium hydroxide solution, yields a *tetrabasic acid*, $C_{22}H_{32}O_8$, which crystallises from dilute acetic acid in prisms, m. p. 189°. The *caesium trihydrogen* salt, $C_{22}H_{31}O_8Cs_3$, crystallises from alcohol in long needles.

The *tetrabasic acid*, $C_{21}H_{30}O_8 = C_{17}H_{26}(CO_2H)_4$, crystallises from hot water in anhydrous, compact prisms or quadratic plates, m. p. 234° (decomp.), or from cold solution in hydrated needles. The needles when dehydrated in a vacuum over sulphuric acid sinter to a transparent mass at about 135°, and this, when further heated, sets to a mass of quadratic plates, m. p. 234° (decomp.). It yields a *mono-caesium* salt, $C_{21}H_{29}O_8Cs$, and is stable towards sodium hydroxide, nitric, sulphuric, and chromic acids, and bromine. The tetrabasic acid is also obtained when the ketonic acid, $CHMe_2 \cdot CO \cdot C_{18}H_{25}(CO_2H)_3$, is oxidised with an acetic acid solution of nitric acid.

J. J. S.

Cholesterol. VII. OTTO DIELS (*Ber.*, 1908, 41, 2596—2600). Compare Dorée and Gardner, *Proc.*, 1908, 24, 173).—The crude *ozonide* of cholesterol contains more oxygen than as stated by Dorée and Gardner. After purification by digestion with cold alcohol, it has the composition $C_{27}H_{46}O_5$, and may be crystallised from hot acetone. It is

stable and does not explode when heated. The purified ozonide is somewhat more stable towards water than the crude, but when heated in sealed tubes at 140—150° it yields a yellow resin and an aqueous solution with a pleasant odour. The close relationship between cholesterol and cholestenone has been already established by Diels and Linn (this vol., i, 164) and Willstätter and Mayer (this vol., i, 636).

J. J. S.

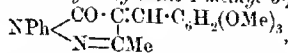
*cyclo*Pen tanecarboxylic Acid and Chlorocyclopentane. NICOLAI D. ZELINSKY (*Ber.*, 1908, 41, 2627—2628).—Chlorocyclopentane, (C_5H_9Cl) , obtained from cyclopentanol and concentrated hydrochloric acid at 110°, has b. p. 114.5—115° (corr.), D_4^{20} 1.0051, n_D^{20} 1.4510, and reacts in ethereal solution with magnesium and carbon dioxide to form cyclopentanecarboxylic acid, b. p. 215.5—216° (corr.) and 104°/11 mm., D_4^{20} 1.0510, n_D^{16} 1.4534, the amide of which has m. p. 179° (corr.).

C. S.

Trimethylgallaldehyde [3:4:5-Trimethoxybenzaldehyde]. Synthesis of Methylsinapic Acid. FERDINAND MAUTHNER (*Ber.*, 1908, 41, 2530—2533. Compare this vol., i, 348).—When heated with aqueous hydrazine hydrate in a sealed tube at 100°, 3:4:5-trimethoxybenzaldehyde forms the *azine*, $N_2[CH \cdot C_6H_2(OMe)_3]_2$, which crystallises in yellow needles, m. p. 195—196°, and gives a red coloration with concentrated sulphuric acid. The oxime of 3:4:5-trimethoxybenzaldehyde has m. p. 83—84° (Semmler, this vol., i, 558). The benzidine derivative, $[C_6H_4 \cdot N \cdot CH \cdot (C_6H_2(OMe)_3)_2]$, crystallises in yellow needles, m. p. 210—211°.

Methylsinapic acid (Gadamer, *Abstr.*, 1898, i, 38) is formed by heating 3:4:5-trimethoxybenzaldehyde with acetic anhydride and sodium acetate at 140—150°. 3:4:5-Trimethoxy- α -methylcinnamic acid, $C_6H_2(OMe)_3 \cdot CH \cdot OMe \cdot CO_2H$, formed together with a neutral oil (trimethoxypropenylbenzene) from 3:4:5-trimethoxybenzaldehyde, propionic anhydride, and sodium propionate at 140—150°, crystallises in long needles, m. p. 157—158°.

4-Phenyl-3:4:5-trimethoxybenzylidene-1-methyl-3-pyrazolone,



obtained by heating the aldehyde with phenylmethylpyrazolone in acetic acid solution, crystallises in red needles, m. p. 141—142°.

Trimethoxybenzylidenebisacetophenone, $C_6H_2(OMe)_3 \cdot CH \cdot (CH_3 \cdot COPh)_2$, m. p. 105—106°. α -Trimethoxyphenyl- β -naphthacetic acid, formed by condensation of trimethylgallaldehyde with pyruvic acid and 6-naphthylamine, is obtained in yellow crystals, m. p. 262—263.

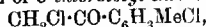
G. Y.

3-Chloro-6-chloroacetyloluene [5-Chloro-*o*-tolyl Chloromethyl Ketone] and Two Chlorodinitrotoluic Acids. FRANZ KUNCKELL (*Ber.*, 1908, 41, 2648—2650).—The reaction between aluminium

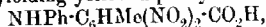
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chloride, *m*-chlorotoluene, and chloroacetyl chloride in carbon disulphide results in the formation of 5-chlorotolyl chloromethyl ketone,



m. p. 90°, from which by means of nitric acid two chlorodinitroketone acids, m. p. 223° and 187—191° respectively, are obtained, the orientations of which are being investigated. The halogen is easily replaced by aniline, yielding yellow diphenylamine derivatives,



m. p. 174° and 216° respectively.

C. S.

Keto-chlorides of 1-Methyl- β -naphthol and their Relation to β -Naphthaquinols. KARL FRIES and E. HEMPELMANN (*Ber.*, 1908, 41, 2614—2626).—When chlorine is passed into a solution of 1-methyl- β -naphthol in slightly diluted acetic acid at 0°, 1-chloro-2-

keto-1-methyldihydronaphthalene, $\text{C}_{10}\text{H}_7\text{Cl}$, $\begin{array}{c} \text{CMeCl}\cdot\text{CO} \\ | \\ \text{CH}=\text{CH} \end{array}$ is ultimately ob-

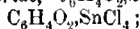
tained as a colourless oil, which cannot be distilled without decomposition, is reduced again to 1-methyl- β -naphthol by stannous chloride, and dissolves in concentrated sulphuric acid with a yellow colour quickly becoming brown. By the use, alternately, of chlorine and of sodium acetate and acetic acid, the following compounds have been obtained in succession: 1:3:4-trichloro-2-keto-1-methyldihydronaphthalene, m. p. 78°; 1:3-dichloro-2-keto-1-methyldihydronaphthalene: 1:3:3:4-tetrachloro-2-keto-1-methyldihydronaphthalene, m. p. 124—125°; 1:3:4-trichloro-2-keto-1-methyldihydronaphthalene, m. p. 85°, and 1:3:3:4:4-pentachloro-2-keto-1-methyldihydronaphthalene, m. p. 103°. Of these compounds, the second and fourth resemble 1-chloro-2-keto-1-methyldihydronaphthalene in their behaviour with concentrated sulphuric acid, and all three dihydronaphthalene compounds may be regarded as the hydrochloric acid esters of 1-methyl-2-naphthaquinol, which shows similar colour reactions. The tetrahydronaphthalene derivatives are stable towards sulphuric acid.

The relation of the preceding derivatives of dihydronaphthalene to the 1-methyl-2-naphthaquinols has been further shown by taking advantage of the reactivity of the chlorine atom in position 1. All three derivatives react with silver acetate to form the corresponding methyl-naphthaquinyl acetates, whilst, in addition, 1:3:4-trichloro-2-keto-1-methyldihydronaphthalene yields 3:4-dichloro-1-methyl-2-naphthaquinol, $\text{C}_{10}\text{H}_5\text{Cl}_2$, $\begin{array}{c} \text{C}(\text{Me}\cdot\text{OH})\cdot\text{CO} \\ | \\ \text{CCl}=\text{CCl} \end{array}$, when warmed in benzene solution with silver nitrite, and the *methoxy*-derivative, m. p. 96°, by treatment with sodium methoxide.

3-Chloro-1-methyl- β -naphthol, $\text{C}_{10}\text{H}_7\text{MeCl}\cdot\text{OH}$, m. p. 60°, obtained by the reduction of 1:3-dichloro-2-keto-1-methyldihydronaphthalene by stannous chloride, forms an *acetate*, m. p. 86°, and regenerates the dichloroketo-chloride by treatment with the calculated amount of chlorine in glacial acetic acid. 3:4-Dichloro-1-methyl- β -naphthol, m. p. 132°, obtained by the reduction of 1:3:4-trichloro-2-keto-1-methyldihydronaphthalene, forms an *acetate*, m. p. 96°.

3-Chloro-1:2-methylnaphthaquinol, $C_6H_4 \begin{matrix} \text{CMe(NO}_2\text{)} \cdot \text{CO} \\ \text{CH} = \text{CCl} \end{matrix}$, m. p. -86° (decomp. just above m. p.), is obtained by passing tenuous fumes into ethereal 3-chloro-1-methyl- β -naphthol at 0° . 4-Dichloro-1:2-methylnaphthaquinol, m. p. $103-104^\circ$ (decomp.), obtained in a similar manner. The two compounds are remarkably stable towards dilute sodium carbonate or alcohol, but by prolonged heating in benzene or glacial acetic acid are converted into 3-chloro-1:2-methylnaphthaquinol, m. p. 70° (acetate, m. p. 133°), and 3:4-dichloro-1:2-methylnaphthaquinol, m. p. 114° (acetate, m. p. 149°), respectively. C. S.

Halochromism of Quinones. KURT H. MEYER (*Ber.*, 1908, 41, 68-2576).—Quinones combine with acids and also with certain metallic halides, forming additive compounds which have a much deeper colour than the original ketones (compare Kehrman and Attisson, *Abstr.*, 1902, i, 229; Vorländer, *Abstr.*, 1905, i, 792). These compounds are unstable, and are decomposed by water, yielding the original quinones. The following compounds are all red in colour: benzoquinone stannic chloride, $C_6H_4O_2 \cdot SnCl_4$, C_6H_6 and



naphthaquinone antimony pentachloride, $C_{10}H_6O_2 \cdot 2SbCl_5$; anthraquinone antimony pentachloride, $C_{14}H_8O_2 \cdot 2SbCl_5$; phenanthraquinone mercuric chloride, $2C_{14}H_8O_2 \cdot HgCl_2$; phenanthraquinone zinc chloride, $H_8O_2 \cdot ZnCl_2$; phenanthraquinone ferric chloride, $3C_{14}H_8O_2 \cdot FeCl_3$. Phenanthraquinone also forms a red additive compound with sulphur oxide at about -50° .

The following compounds have a green colour: phenanthraquinone stannic chloride, $C_{14}H_8O_2 \cdot SnCl_4$, which turns red on exposure to the air; phenanthraquinone aluminium chloride, $C_{14}H_8O_2 \cdot AlCl_3$. The absorption curves for chloroform solutions of the additive compounds of a quinone with an acid and with a metallic halide are very similar. Ketones also form coloured additive compounds with metallic halides. Benzophenone antimony pentachloride, $COPh_3 \cdot 2SbCl_5$, crystallises in yellow needles, and benzil stannic chloride, $C_{14}H_{10}O_2 \cdot SnCl_4$, in yellow plates.

Triphenylchloromethane absorbs hydrogen chloride at -60° , yielding a yellow additive compound, $CPh_3Cl \cdot 6HCl$; the bromo-derivative yields a similar compound with hydrogen bromide.

The introduction of halogen into the quinone molecule, as, for example, in tetrachloro-*o*- and -*p*-benzoquinone, inhibits the formation of additive compounds with metallic salts. J. J. S.

Quinonoid Compounds. XVI. Two Forms of *o*-Quinones. EDWARD WILLSTÄTTER and FRITZ MÜLLER (*Ber.*, 1908, 41, 2580-2586; compare *Abstr.*, 1905, i, 144; this vol., i, 475).—A colourless modification of *o*-benzoquinone is obtained when the oxidation of catechol is carried out rapidly (fifteen seconds) at low temperatures.

It is necessary to wash the silver oxide well and to dry it by means of acetone and ether. The colourless crystals are obtained when the

filtered ethereal solution is mixed with light petroleum, or cooled to -15° to -20° . The ethereal solutions are green, but the crystals are colourless. The compound has quinonoid properties, but is extremely unstable, and is either transformed into the red modification or decomposes.

When the pure red compound is dissolved in ether and the solution cooled, a mixture of the colourless and red crystals is obtained, so that in the solution the two compounds are present in a state of equilibrium.

The ketonic formula $O:C_6H_4:O$ is assigned to the red compound, and the formula $C_6H_4 \begin{smallmatrix} \diagup O \\ \diagdown O \end{smallmatrix}$ to the colourless.

J. J. S.

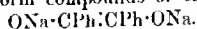
The Claisen Condensation. II. Mechanism of the Reaction. J. BISHOP TINGLE and ERNEST E. GORSLINE (*Amer. Chem. J.*, 1908, 40, 46—88. Compare Abstr., 1907, i, 498).—The authors have carried out a number of experiments with the object of ascertaining the influence of change of conditions on the Claisen condensation between certain ketones and esters, and, hence, on the yield of diketone. The principal results obtained are as follows.

With camphor as the ketone, calcium or sodamide is practically useless as a condensing agent unless alcohol is added, and, even then, a relatively high temperature is required (compare Claisen, Abstr., 1905, i, 286).

The nature of the "solvent product," or the residue left after the distillation of the solvent, varies in different cases. With condensations between camphor and ethyl oxalate in presence of sodium or sodamide, considerable quantities of camphoroxalic acid can be extracted from the solvent product, and the same holds when camphor and ethyl cinnamate are condensed by means of either of these agents. When, however, calcium is used, no trace of the condensation product is found in the solvent product.

The reaction is markedly influenced by the nature of the ketone or aldehyde employed, and also by that of the ester, and this influence is probably not confined to the velocity, but, in some cases, extends to the actual mechanism of the reaction. The readiness with which the reaction takes place is increased by the proximity of two carbethoxyl groups, and there are indications that the mechanism of the reactions resulting in the formation of diketones varies in the two cases of aliphatic and aromatic esters.

Experiments on the acetoacetic ester condensation, in which small quantities of ether, light petroleum, or pyridine were used as solvents, show that the catalytic influence of ether and pyridine on the velocity of the reaction is appreciable. No evidence could be obtained to show that ether or a tertiary base has any catalytic action when sodium reacts with esters to form compounds of the class



It seems probable that the two reactions take place simultaneously, and that in the presence of solvents the reaction $2CH_3 \cdot CO_2Et + 4Na = ONa \cdot CMe : CMe \cdot ONa + 2NaOEt$ preponderates considerably.

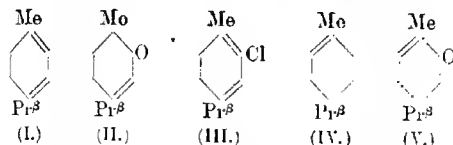
If the explanation of the Claisen condensation given by its discoverer (Abstr., 1895, i, 62) is correct, sodium ethoxide should be an excellent accelerator, and this is found to be the case, the addition of a little alcoholic sodium ethoxide accelerating to a marked degree the reactions between camphor and the esters of various acids in presence of light petroleum as solvent. Absolute alcohol is a still more effective accelerating agent, but sodium ethoxide free from alcohol affects the speed of the reaction very little, if at all. A striking fact is the very great reduction in the yield of diketone occurring when alcohol or alcoholic sodium ethoxide is added.

When the esters of the aliphatic series are condensed with camphor, the use of more than one atomic proportion of sodium does not increase the yield of the diketone. The catalytic agent does not accelerate the reaction between sodium and the ester, or that between sodium and camphor. Sodium camphor acts as a feeble condensing agent.

The authors' results indicate that, taken in connexion with the action of sodium on esters and with the catalytic influence of ether and the tertiary bases, Michael's explanation of the Claisen condensation (Abstr., 1901, i, 123; 1905, i, 506) is the most satisfactory.

T. H. P.

Constitution of Terpinene. CARL D. HARRIES and RIKO MAJIMA (*Ber.*, 1908, 41, 2516—2529).—Amenomija (Abstr., 1905, i, 803) suggested that carvenene (I) might be identical with terpinene, and attempted to prepare it from carvenone (II) in the same manner as Harries and Johnson obtained α -phellandrene (IV) from Δ^3 -menthene-ketone (V), but was unable to reduce the intermediate chloro-compound III).

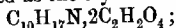


It is now found that when carvenone is converted by way of its oxime into 2-amino- Δ^3 -menthene, and the phosphate of this base is distilled, a single hydrocarbon, which must be carvenene, is obtained, but if the ketone is converted into its hydroxylamino-oxime (VI), and this into 2:4-diaminomenthane (VII), distillation of the phosphate leads to the formation of a mixture of hydrocarbons.

The relation of carvenone to terpinene is discussed (compare Wallach, Abstr., 1907, i, 64; Semmler, Abstr., 1907, i, 714).

Carvenone forms two oximes, one of which, m. p. 90—92° (Wallach, Abstr., 1894, i, 44; 1895, i, 672), forms a hydrochloride, m. p. 13—114°, crystallising from ether-alcohol. The other oxime is an

oil, and forms a *hydrochloride*, m. p. 105—113°, which remains dissolved in the ether-alcoholic mother liquor. Reduction of carvenone-oxime with zinc dust in acetic acid solution leads to the formation of the *imine*, which is isolated as the crystalline *oxalate*,



this is readily hydrolysed by water, forming ammonium oxalate and carvenone. The free imine, b. p. 105°/12 mm., decomposes at the ordinary temperature, and yields benzamide when benzoylated by the Schotten-Baumann method. Contrary to Wallach and Boedecker's statement (Abstr., 1907, i, 943), carvenoneoxime cannot be formed intermediately in the reduction of terpinene nitrosite, as, although hydrolysed by sulphuric acid, it is stable towards boiling glacial acetic acid.

2-Amino- Δ^3 -menthene (*carvenylamine*), $\text{C}_{10}\text{H}_{19}\text{N}$, prepared by reduction of carvenoneoxime by means of aluminium amalgam in ethereal solution, is separated from the imine formed simultaneously by hydrolysis of the latter with hydrochloric acid. It has b. p. 86—89°/10 mm., D_4^{20} 0.8762, and n_D^{20} 1.46966. When boiled with acetic anhydride, it forms a *syrup*, which decolorises bromine. The *benzoyl* and *phenylcarbamide* derivatives are syrups. The *hydrochloride*, *nitrate*, and *acid oxalate*, m. p. about 120°, are described.

Carvenene (Δ^{13} -menthadiene), $\text{C}_{10}\text{H}_{16}$, b. p. 68—70°/15 mm., D_4^{20} 0.8453, n_D^{20} 1.48379, prepared by distillation of carvenylamine phosphate, has a faint odour of lemons, and forms terpinene nitrosite, m. p. 155—156°.

Carvenone hydroxylamino-oxime, prepared from dihydrocarvone or from terpinene nitrosite, has m. p. 162—162.5° (167—168°: Tiemann and Semmler, Abstr., 1899, i, 224), and when treated with mercuric oxide forms the *nitroso-oxime*, $\text{C}_{10}\text{H}_{18}\text{O}_2\text{N}_2$, blue crystals, m. p. 113—115°, together with a white, sparingly soluble, crystalline substance.

2:4-Diaminomenthane, $\text{C}_{10}\text{H}_{22}\text{N}_2$, prepared by reduction of the hydroxylamino-oxime with sodium and alcohol, is an oil, b. p. 121.5°/12 mm., D_4^{20} 0.9192, n_D^{20} 1.4848. The *hydrochloride*, *sulphate*, *nitrate*, *platinichloride*, *oxalate*, *benzoyl* derivative, and *phenylcarbamide* derivative, m. p. 220—222°, are described. On distillation, the phosphate of the diamine yields a mixture of hydrocarbons, b. p. 62—65°/11 mm., D_4^{20} 0.8611, n_D^{20} 1.48802, which gradually forms a syrup. The fresh mixture yields small amounts of terpinene nitrosite. The action of sodium nitrite on the diamine hydrochloride leads to the formation of an oil, b. p. 65—100°/12 mm., which does not yield terpinene nitrosite.

G. V.

Components of Ethereal Oils. Elimination of Methoxy-groups in the para-Position with Respect to Allyl or Propenyl Radicles. FRIEDRICH W. SEMMLER (*Ber.*, 1908, 41, 2556—2557. Compare this vol., i, 557, 558, 664).—The product obtained by reducing elemicin or, even better, isoelemicin with sodium and alcohol is shown to have the composition $\text{C}_{11}\text{H}_{16}\text{O}_2$, and is 3:5-dimethoxy-1-n-propenylbenzene, since it yields 3:5-dimethoxybenzoic acid when oxidised. The reduction thus consists in the conversion of the propenyl to a

propyl group, and the elimination of the methoxy-radicle which was in the para-position with respect to the propenyl group. The propenyl group thus behaves in much the same manner as the keto-group (compare Kostanecki, this vol., i, 359). J. J. S.

Position of Bromine Atoms in Derivatives of Methronic Acid. HYPOLYT TREPHILIEFF (*Ber.*, 1908, 41, 2543—2544).—The tetrabromo-derivative of methronic acid described recently (Abstr., 1907, i, 1063) may have the constitution (I)
$$\text{O} \begin{array}{c} \text{C}(\text{CHBr}_2) \\ \text{C}(\text{CBr}_2 \cdot \text{CO}_2\text{H}) \end{array} \begin{array}{c} \text{C}(\text{CHBr}_2) \\ \text{C}(\text{CO}_2\text{H}) \end{array} \text{CH}$$

or (II)
$$\text{O} \begin{array}{c} \text{C}(\text{CBr}_3) \\ \text{C}(\text{CHBr} \cdot \text{CO}_2\text{H}) \end{array} \begin{array}{c} \text{C}(\text{CO}_2\text{H}) \\ \text{C}(\text{CH} \cdot \text{CO}_2\text{H}) \end{array} \text{CH}$$
. It is now found that the action

of bromine on ethyl phenithronate leads to the formation of a *dibromo*-derivative, $\text{C}_{15}\text{H}_{12}\text{O}_3\text{Br}_2$, which is obtained in yellow crystals, and on 3-carboxy-2-methylfuran-4-acetic acid, $\text{O} \begin{array}{c} \text{CH} \\ \text{C}(\text{CH}_2 \cdot \text{CO}_2\text{H}) \end{array} \begin{array}{c} \text{CH} \\ \text{C}(\text{CO}_2\text{H}) \end{array} \text{CH}$ (Feist, Abstr., 1899, i, 675), to that of a *tribromo*-derivative, $\text{C}_8\text{H}_5\text{O}_3\text{Br}_3$, which crystallises from acetic acid. Both these derivatives decompose without melting when heated. Bromine does not react, on the other hand, with the methyl groups of 3:4-dimethylfurandicarboxylic acid; hence it is considered that the tetrabromo-derivative of methronic acid has the constitution (I). G. Y.

Constitution of Methronic Acid. HYPOLYT TREPHILIEFF (*Ber.*, 1908, 41, 2545—2546. Compare Abstr., 1906, i, 528).—The fraction, b. p. 300—305°, obtained from the product of the action of sodium succinate on ethyl acetoacetate (Fittig and Hantzsch, Abstr., 1889, 126), contains ethyl methronate, which on hydrolysis yields methronic acid. This, when treated with aqueous ammonia at 320°, forms dimethylpyrrole, b. p. 165°.

When exposed to bromine vapour for two to three months, 2:5-dimethylfuran-3-carboxylic acid forms a *tetrabromo*-derivative, $\text{C}_7\text{H}_4\text{O}_3\text{Br}_4$, which is obtained as a crystalline mass. G. Y.

Crystallography of the Fulgides. ZOLTÁN TOBORFFY (*Zeitsch. Krist. Min.*, 1908, 45, 155—181).—Crystallographic details are given concerning thirty-nine fulgide compounds recently prepared by Stobbe (Abstr., 1905, i, 857; 1906, i, 960). L. J. S.

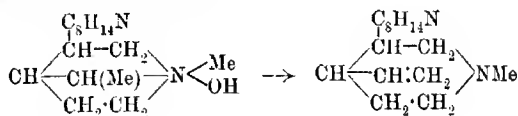
Reactions of Hordenine Based on the Constitution of this Substance. GEORGES DENIGÈS (*Bull. Soc. chim.*, 1908, [iv], 3, 786—792).—The constitution assigned by Léger to this alkaloid (Abstr., 1906, i, 204, 761; 1907, i, 151, 234, 337) indicates that it contains residues of *p*-cresol and of trimethylene, and the following reactions characteristic of substances containing these residues confirm Léger's formula.

When a drop of a solution of hordenine sulphate is placed on a glass slip and a drop of iodine solution is added, characteristic crystals of a brown iodo-compound separate, which are visible under the microscope. Trimethylamine yields a crystalline derivative under the same conditions, as does also choline.

Hordenine (0.02—0.03 gram) dissolved in 4 c.c. of acetic acid gives, on boiling with four drops of formaldehyde solution and the subsequent addition of 3 c.c. of sulphuric acid, a green coloration, which rapidly deepens. Tyrosine, under the same conditions, gives a red coloration, which, on gently warming, passes into green. Under somewhat similar conditions, *p*-cresol also gives a green coloration. Similar green colorations are obtained with tyrosine or hordenine when formaldehyde solution is replaced by paraldehyde. Precise instructions for the application of these tests under various conditions are given in the original. It is suggested that Aloy and Rabaut's tyrosine colour reaction with bromine and ammonia solution (this vol., i, 341) is probably due to the presence of the *p*-cresol residue, *p*-Cresol gives with bromine water, followed by ammonia, a yellow coloration, passing into orange, and hordenine an intense yellow.

T. A. H.

Sparteine. Transformation of *iso*Sparteine into α -Methylsparteine. AMAND VALEUR (*Compt. rend.*, 1908, 147, 127—129. Compare this vol., i, 43, 44, 103, 206).—When the solution of α -methylsparteine, after isomerisation by boiling with dilute sulphuric acid, is evaporated in a vacuum, crystals of *isosparteine methosulphate*, $C_{14}H_{26}N_2Me.HSO_4.9H_2O$, are formed, having $[\alpha]_D - 13.65^\circ$. This salt is decomposed by baryta with the formation of *α -methylisosparteinium hydroxide*, which yields a precipitate of *isosparteine methiodide* with potassium iodide, and is quantitatively transformed into α -methylsparteine by heating in a vacuum below 100° . Adopting the author and Moureu's constitutional formula for sparteine, the last change may be represented thus:



G. B.

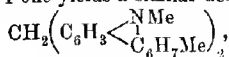
Organic and Fused Salts (Conductivity). CARL SCHALL (*Zeitsch. Elektrochem.*, 1908, 14, 397—405).—*Quinoline *n*-butiodide*, m. p. $175.5-176.1^\circ$, and *isobutiodide*, m. p. $159-159.5^\circ$, were prepared. The following salts were also prepared in a very pure state: Pyridine methiodide dibromide, m. p. $68-69^\circ$; quinoline hydriodide di-iodide, m. p. 67° ; quinoline methiodide di-iodide, m. p. $108.6-109.6^\circ$; quinoline methiodide tetra-iodide, m. p. $72-73^\circ$; quinoline ethiodide di-iodide, m. p. $43-45^\circ$; quinoline propiodide di-iodide, m. p. 60° ; quinoline *n*-butiodide di-iodide, m. p. 60.7° , and quinoline *isobutiodide* di-iodide, m. p. 85.6° . The *isopropyl* salt could not be obtained pure. The di-iodides of the hydriodides and methiodides show slight dissociation at their melting points; the other salts evolve mere traces of iodine or none. The electrical conductivity of the *n*-propyl, *n*-*is* reduced *isobutyl* compounds was measured for the fused anhydrous
at several temperatures.

T. E.

Dihydrazines. II. Diphenylmethanedimethylhydrazine and Cyclic Ketones. JULIUS VON BRAUN (*Ber.*, 1908, 41, 2604—2607. Compare this vol., i, 700).—*cyclo*Hexanone (2 mols.) reacts with an acetic acid solution of diphenylmethanedimethyldihydrazine (1 mol.) in the presence of a little sulphuric acid, yielding the *bistetrahydro-*dicarbazole of the diphenylmethane series, $\text{CH}_2(\text{C}_6\text{H}_5 \angle \text{C}^{\text{NMe}} \text{C}_6\text{H}_5)_2$.

It is best purified by solution in pyridine and precipitation with alcohol, has m. p. 175°, and dissolves in concentrated acids.

1-Methyl*cyclo*hexan-4-one yields a similar derivative,



m. p. 143°, and the corresponding *m*-compound, an isomeride, m. p. 200°.

1-Methyl*cyclo*hexan-3-one, menthone, 1:3-dimethyl*cyclo*hexen-5-one, and sabinaketone do not react with diphenylmethanedimethyldihydrazine. It thus appears that only those cyclic ketones which contain the grouping $\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot$ are capable of reacting with the dihydrazine.

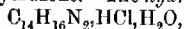
*cyclo*Pentanone does not react so readily as *cyclo*hexanone, and does not yield a pure product. J. J. S.

Reduction of Phenylhydrazones in Alkaline Solution. OSKAR SCHLENK (*J. pr. Chem.*, 1908, [ii], 78, 49—63).—Whilst the action of sodium amalgam on phenylhydrazones in acid solution leads to the formation of amines, $\text{R}\cdot\text{CH}\cdot\text{N}\cdot\text{NHPh} \rightarrow \text{R}\cdot\text{CH}_2\cdot\text{NH}_2 + \text{NH}_2\text{Ph}$ (Tafel, *Abstr.*, 1887, 975), the reduction in alkaline solution allows, in the case of phenylhydrazones of aromatic aldehydes, of the isolation of the intermediate hydrazine, $\text{R}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{NHPh}$. In the following alkaline reductions, part of the excess of sodium hydroxide was neutralised by a current of carbon dioxide.

β -Phenylbenzylhydrazine, $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{NHPh}$, formed by the action of sodium amalgam on phenylbenzylidenehydrazine in boiling alcoholic solution, crystallises in colourless rhombohedra, m. p. 35°, b. p. 290° (decomp.) (m. p. 155.5°: Schlömann, *Abstr.*, 1893, i, 452), reduces Fehling's solution when heated and silver solutions at the ordinary temperature, and, on exposure to air, changes into a yellow mass, from which phenylbenzylidenehydrazine gradually crystallises. The *hydrochloride*, $\text{C}_{15}\text{H}_{11}\text{N}_2\cdot\text{HCl}$, forms white leaflets, m. p. 205°; the *hydrogen oxalate*, $\text{C}_{15}\text{H}_{11}\text{O}_4\text{N}_2$, m. p. 190°. The action of oxidising agents on β -phenylbenzylhydrazine leads to the formation of phenylbenzylidenehydrazine, and the prolonged action of mercuric oxide to that of the yellow tetrazone. On reduction with sodium amalgam and acetic acid, β -phenylbenzylhydrazine yields aniline and benzylamine. The *acetyl* derivative, $\text{CH}_2\text{Ph}\cdot\text{NAc}\cdot\text{NHPh}$, prepared by adding the hydrazine to a cooled solution of zinc chloride in acetic anhydride, crystallises in prisms, m. p. 91°, reduces Fehling's solution only on prolonged boiling, and forms a *nitroso*-derivative, $\text{CH}_2\text{Ph}\cdot\text{NAc}\cdot\text{NPh}\cdot\text{NO}$, crystallising in yellow rhombohedra, m. p. 84°. This gives Liebermann's reaction, and on reduction with zinc dust and acetic acid yields phenylhydrazine and

acetylbenzylamine. The *benzoyl* derivative, $\text{CH}_2\text{Ph}\cdot\text{NBz}\cdot\text{NHPh}$, formed by the action of benzoyl chloride on the hydrazine in cooled ethereal solution, crystallises in colourless needles, m. p. 121°–122°, and yields a *nitroso*-derivative, $\text{C}_{20}\text{H}_{17}\text{O}_2\text{N}_3$, crystallising in yellow needles, m. p. 102°. The *dibenzoyl* derivative, $\text{CH}_2\text{Ph}\cdot\text{N}(\text{Bz})\cdot\text{N}(\text{Bz})\text{Ph}$, formed by the Schotten-Baumann method, crystallises in hexagonal prisms, m. p. 131°.

p-Tolylbenzylidenehydrazine, $\text{C}_{14}\text{H}_{14}\text{N}_2$, crystallises from alcohol in colourless needles, m. p. 125°, becomes intensely red on exposure to air, and on reduction with sodium amalgam in boiling alcoholic solution yields β -*p*-tolylbenzylhydrazine, $\text{C}_{14}\text{H}_{16}\text{N}_2$, which is obtained as a viscid, yellow oil, b. p. 212°/17 mm., reduces Fehling's solution when heated, and on exposure to air or when treated with oxidising agents again forms the hydrazone. The *hydrochloride*,



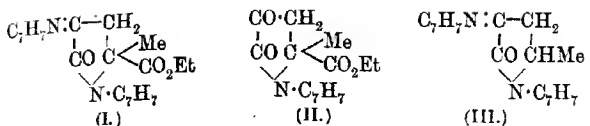
long, thin needles, m. p. 185° (decomp.), loses H_2O slowly in a vacuum. The *benzoyl* derivative, $\text{C}_{21}\text{H}_{20}\text{ON}_2$, crystallises in white needles, m. p. 159°.

Reduction of the phenylhydrazone of benzylideneacetone by means of sodium amalgam and acetic acid in alcoholic solution leads to the formation of γ -amino- α -phenylbutane, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{NH}_2$, which is obtained as a colourless oil, b. p. 222°/716 mm., D_4^{20} 0.9289, has a slight ammoniacal odour and a strong alkaline reaction, is only sparingly soluble in water, and absorbs carbon dioxide from the air, forming a crystalline carbonate. The *hydrochloride*, needles, m. p. 144°; the *platinichloride*, $(\text{C}_{10}\text{H}_{15}\text{N})_2\text{H}_2\text{PtCl}_6$, yellow leaflets, decomp. 220°; the *sulphate*, m. p. 255° (decomp.); the *hydrogen oxalate*, m. p. 110°; the *oxalate*, m. p. 232°; the *benzoyl* derivative, needles, m. p. 107°. The action of sodium nitrite on the base in hot hydrochloric acid solution leads to the formation of α -phenyl- β -butylene and a product of high boiling point, which may be the corresponding alcohol or a polymeride of the butylene. When heated with sodium amalgam in alcoholic solution at 55°, the phenylhydrazone of benzylideneacetone yields the *phenylhydrazone* of benzylacetone, $\text{C}_{13}\text{H}_{13}\text{N}_2$, which crystallises in colourless leaflets, m. p. 59°, is unstable, changing to a reddish-yellow oil, and has slight basic properties.

The alkaline reduction of benzilosazone leads to the formation of diphenylhydroxyethylamine, diphenylethylenediamine, m. p. 107°–110° (90°–92°: Feist, Abstr., 1894, i, 196; 120°: Grossmann, Abstr., 1889, 1191), and tetraphenylpyrazine, m. p. 244°. G. Y.

Mechanism of the Synthesis of Cyclic Nitrogen Compounds.

Action of Ethyl Pyruvate on *p*-Toluidine. Louis J. SIMON (*Compt. rend.*, 1908, 147, 125–127. Compare this vol., i, 296, 687).—The ester, $\text{C}_{10}\text{H}_{11}\text{O}_3\text{N}_2$ (I), previously obtained by the interaction of *p*-toluidine and ethyl pyruvate, is hydrolysed by cold concentrated sulphuric acid to a *substance*, $\text{C}_{10}\text{H}_{15}\text{O}_4\text{N}$ (II), m. p. 152°, and is transformed by alcoholic potassium hydroxide into a *substance*, $\text{C}_{12}\text{H}_{20}\text{ON}_2$, m. p. 190°. The three substances may be represented thus:



Simultaneously with the substance (I), there is also formed a more soluble substance, $\text{C}_{24}\text{H}_{30}\text{O}_4\text{N}_2$, m. p. 142° , which may be represented thus: $\text{C}_7\text{H}_7\cdot\text{NH}\cdot\text{CMe}(\text{CO}_2\text{Et})\cdot\text{CH}_2\cdot\text{C}(\text{CO}_2\text{Et})\text{:N}\cdot\text{C}_7\text{H}_7$, and is transformed by alcoholic potassium hydroxide into an acid, m. p. 265° (decomp.), in all probability 4:6-dimethylquinoline-2-carboxylic acid.

G. B.

Action of Nitric Acid on 2:6-Dioxypyrimidines. Nitro-hydroxyhydrothymine. XXX. TREAT B. JOHNSON (*Amer. Chem. J.*, 1908, 40, 19—36. Compare this vol., i, 692).—The author has not been able to obtain Stendel's nitrothymine (*Abstr.*, 1901, i, 434), which he regards as a secondary decomposition product, and not as a simple thymine derivative.

With fuming nitric acid (D 1.5) at the ordinary temperature, uracil gives 5-nitrouracil; 5-bromouracil, 5-bromo-5-nitro-4-hydroxyhydrouracil (compare Behrend, *Abstr.*, 1887, i, 919); 5-chlorouracil, 5-chloro-5-nitro-4-hydroxyhydrouracil, and thymine, 5-nitro-4-hydroxyhydrothymine. The formation of these hydropyrimidines involves a direct addition of nitric acid to the double linking between the 4- and 5-positions of the pyrimidine ring (compare Behrend, *Annalen*, 1885, 229, 1—44).

The reduction of 5-bromo-5-nitro-4-hydroxyhydrouracil by means of tin and hydrochloric acid yields Behrend's hydroxyxanthine (*loc. cit.*).

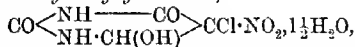
5:5-Dichloro-4-hydroxyhydrouracil, $\text{CO} \begin{array}{c} \text{NH} \text{---} \text{CO} \\ \text{NH}\cdot\text{CH}(\text{OH}) \end{array} \text{CCl}_2\cdot\text{H}_2\text{O}$,

prepared by the action either of chlorine water or of potassium chlorate and hydrochloric acid on uracil, crystallises from water in large prisms, m. p. $212\text{--}215^\circ$ (decomp.).

5-Chlorouracil, $\text{CO} \begin{array}{c} \text{NH}\cdot\text{CO} \\ \text{NH}\cdot\text{CH} \end{array} \text{CCl}$, prepared by the action of

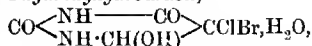
chlorine water on uracil or by reducing the preceding compound by means of tin and hydrochloric acid, crystallises from water in prisms, m. p. $300\text{--}305^\circ$.

5-Chloro-5-nitro-4-hydroxyhydrouracil,



obtained by the action of fuming nitric acid (D 1.5) on 5-chlorouracil, separates in hard, prismatic crystals, which decompose with effervescence at $150\text{--}160^\circ$.

5-Chloro-5-bromo-4-hydroxyhydrouracil,



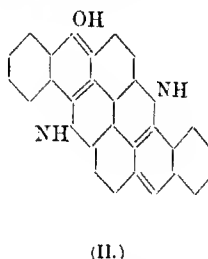
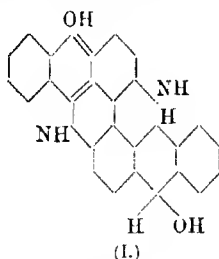
prepared from 5-bromouracil or 5-chlorouracil by the action of chlorine or bromine water respectively, crystallises from bromine water in prisms, decomposing with effervescence at $195\text{--}200^\circ$, and yields 5-chlorouracil when boiled with alcohol.

The action of bromine water on 5-iodouracil yields 5:5-dibromo-4-hydroxyhydrouracil (compare Wheeler and Johnson, *Abstr.*, 1907, ii, 826).

5-Nitro-4-hydroxyhydrothymine, $\text{CO} \begin{array}{c} \text{NH} \text{---} \text{CO} \\ \text{NH} \cdot \text{CH}(\text{OH}) \end{array} \text{CMe} \cdot \text{NO}_2$, exists in the following two modifications: (1) the α -form, obtained by dissolving thymine in fuming nitric acid, separates in triclinic prisms or blocks [W. E. FORD: $a:b:c = 0.578:1:0.420$; $\alpha = 107^\circ 35'$, $\beta = 100^\circ 25'$, $\gamma = 80^\circ 59'$], m. p. 183° (decomp.), and dissolves in water, giving an acid solution, or in alcohol. (2) The β - or unstable modification, obtained under certain conditions when thymine is dissolved in fuming nitric acid, crystallises from water or alcohol in prisms, m. p. $230\text{--}235^\circ$, and gradually changes into the β -form when kept at the ordinary temperature. Both modifications yield thymine when reduced with tin and hydrochloric acid.

T. H. P.

Indanthren and Flavanthren. XI. Reduction Products of Flavanthren. ROLAND SCHOLL and W. NEOVIUS (*Ber.*, 1908, 41, 2534—2540. Compare this vol., i, 696).—Energetic reduction of flavanthren with zinc dust and sodium hydroxide leads to the formation of α -hexahydroflavanthren (I) and flavantrihol (II):



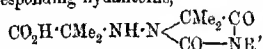
α -Hexahydroflavanthren hydrate is obtained as a stable, blackish-blue powder, $\text{C}_{28}\text{H}_{18}\text{O}_2\text{N}_2 \cdot \text{H}_2\text{O}$, which loses H_2O at 160° , dissolves in alcohol to a bluish-red, or if highly dilute to a violet, solution with brilliant, scarlet fluorescence, but in nitrobenzene to a non-fluorescent solution, forms fluorescent solutions in alcoholic alkalis or concentrated acids, and dyes unmordanted wool in an alkaline bath red, becoming greenish-blue on treatment with acids, and violet with water. On prolonged heating with zinc dust in alkaline solution, α -hexahydroflavanthren hydrate is converted into flavantrihol hydrate, whilst the anhydrous hexahydro-compound forms anhydrous flavantrihol when heated at 300° in a current of carbon dioxide. On treatment with a current of air in alkaline solution, the hexahydro-compound is oxidised to flavanthren.

Flavantrihol hydrate, $\text{C}_{28}\text{H}_{16}\text{ON}_2 \cdot \text{H}_2\text{O}$, forms a blue, voluminous precipitate, becoming blackish-blue when dried, loses H_2O at 160° , is less soluble than α -hexahydroflavanthren hydrate, forms red solutions with olive-green fluorescence in organic solvents, except nitrobenzene,

in which it is not fluorescent, gives coloured solutions with reddish-brown fluorescence in concentrated acids, and dyes unmordanted wool violet-red, becoming green with acids, and blue with water. Flavanthrinol is not oxidised by air at the ordinary temperature, but, on treatment with ferricyanide or when heated in air, yields flavanthren.

G. Y.

Desulphurisation of Thiohydantoins. JAMES R. BAILEY and C. P. RANDOLPH (*Ber.*, 1908, 41, 2404—2505).—Bailey observed (Abstr., 1904, i, 826) that 1-carboxyisopropylamino-5:5-dimethyl-2-thiohydantoins, $\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{NH}\cdot\text{N}\cdot\text{N}\cdot\text{C}(\text{CS})\cdot\text{CO}$, having R = an aliphyl or aryl group in position 3, are readily converted by means of mercuric oxide into the corresponding hydantoins,



which on treatment with bromine water are oxidised, forming the azo compounds, $\text{CO}\cdot\text{CMe}_2\cdot\text{NH}\cdot\text{N}\cdot\text{N}\cdot\text{N}\cdot\text{N}\cdot\text{C}(\text{CO})\cdot\text{CO}$, containing the tetrazone grouping $\cdot\text{N}\cdot\text{N}\cdot\text{N}\cdot\text{N}\cdot$. It is found now that the desulphurisation and the oxidation to the tetrazone take place in one operation when the thiohydantoin is treated with bromine water. These observations led to the study of the desulphurisation of thiohydantoins in general. Although the statements of Aschan (Abstr., 1884, 907) and of Marekwald, Neumark, and Stelzner (Abstr., 1892, 149) suggest that this desulphurisation takes place with ease, it is found that the thiohydantoins studied other than those already mentioned are not converted into hydantoins by the action of mercuric oxide. On the other hand, the desulphurisation does take place readily when the alkali salts of the thiohydanitoic acids are treated with mercuric oxide, the resulting hydantoates being readily converted into the hydantoins. Thus 3-methylhydantoin and 3-ethylhydantoin are formed by heating potassium methylthiohydanitoate and ethylthiohydanitoate respectively with mercuric oxide in aqueous solution.

Whilst 1-carboxyisopropylamino-3-phenyl-5:5-dimethyl-2-thiohydantoin is readily desulphurised by mercuric oxide, 3-phenyl-5:5-dimethylhydantoin is not obtained by the action of mercuric oxide on

the thiohydantoin, $\text{NH}\cdot\text{C}(\text{CS})\cdot\text{CO}$, but, on the other hand, all thiohydantoins derived from α -aminoisobutyric acid are desulphurised normally by bromine water. Thiohydantoins derived from glycine or alanine, that is, containing one or two hydrogen atoms in position 5, when treated with bromine water, yield sulphuric acid and halogen-substitution products of the hydantoins (compare Andreasch, Abstr., 1902, i, 157).

Ethylthiohydanitoic acid, $\text{C}_8\text{H}_{10}\text{O}_3\text{N}_2$, prepared from the hydantoin, has m. p. 132° (decomp.).

3-Allylhydantoin, $\text{C}_6\text{H}_8\text{O}_3\text{N}_2$, crystallises in thin needles, m. p. 78° .

3-p-Tolylthiohydanitoic acid, $\text{C}_{10}\text{H}_{12}\text{O}_3\text{N}_2$, separates from alcohol in crystals, m. p. 203° (decomp.); the *ethyl* ester, m. p. 166° . 3-p-Tolyl-

hydantoin crystallises in needles, m. p. 211° (205°: Quenda, Abstr., 1892, 828).

Phenylmethylhydantoic acid, prepared by the action of mercuric oxide on the corresponding potassium thiohydantoate, has m. p. 170° (decomp.), and on treatment with acids is converted into 3-phenyl-5-methylhydantoin.

The following hydantoins were prepared by the action of bromine water on the corresponding thiohydantoins, sulphuric acid being formed to the extent of about 66% of the theoretical amount. Thiohydantoins were formed from α -aminoisobutyronitrile by Marckwald, Neumark, and Stelzner's method (*loc. cit.*). The data in brackets after the m. p.'s are those given by Marckwald, Neumark, and Stelzner.

3-Phenyl-5:5-dimethylthiohydantoin crystallises in prisms, m. p. 174° (67°); the methyl ether, $C_{11}H_{11}ON_2SMe$, m. p. 96° (viscid liquid), forms a platinichloride, $(C_{11}H_{11}ON_2S)_2H_2PtCl_6$, decomp. about 240° (132°), and a picrate, $C_{12}H_{14}ON_2S \cdot C_6H_3O_7N_3$, m. p. 194° (174°). 3-Phenyl-5:5-dimethylhydantoin, $C_{11}H_{12}O_2N_2$, crystallises in broad prisms, m. p. 171°, and is obtained also from α -aminoisobutyronitrile and phenylcarbimide.

3:5:5-Trimethylthiohydantoin, $C_8H_{10}ON_2S$, crystallises in microscopic prisms, m. p. 145° (53°), and appears to form a sparingly soluble compound with mercuric oxide, blackening not taking place. 3:5:5-Trimethylhydantoin, $C_8H_{10}O_2N_2$, crystallises in long prisms, m. p. 149°.

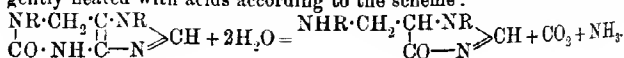
3-p-Tolyl-5:5-dimethylthiohydantoin, $C_{12}H_{14}ON_2S$, forms needles, m. p. 223° (85°). 5-p-Tolyl-5:5-dimethylhydantoin, $C_{12}H_{14}O_2N_2$, m. p. 175°.

G. Y.

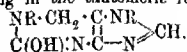
Thiohydantoins and Bases derived from These. JAMES R. BAILEY and C. P. RANDOLPH (*Ber.*, 1908, 41, 2505—2508).—The authors draw attention to, and discuss some possible explanations of, the differences in the properties of the thiohydantoins described by Marckwald, Neumark, and Stelzner (Abstr., 1892, 149), and of those prepared by the same methods by themselves (preceding abstract). The constitution of the thiohydantoins now obtained is confirmed by the conversion of 3-phenyl-5:5-dimethyl-2-thiohydantoin into 3-phenyl-5:5-dimethylhydantoin, which is formed also by condensation of α -aminoisobutyronitrile with phenylcarbimide, and by the action of sulphuric acid on

1-azo-3-phenyl-5:5-dimethylhydantoin, $N_2 \left[N \begin{array}{c} \text{CMe}_2 \cdot \text{CO} \\ \text{CO} - \text{NPh} \end{array} \right]_2$ G. Y.

Hydrolysis of Xanthines and Deoxyxanthines. JULIUS TAFEL and RUDOLF MAYER (*Ber.*, 1908, 41, 2546—2556. Compare Abstr., 1907, i, 984).—It has been observed that, whilst some deoxyxanthines decompose readily with evolution of carbon dioxide when heated with dilute acids, others exhibit much greater stability. A systematic study has now shown that xanthine itself and all methylated xanthines which are not methylated in position 3 are readily hydrolysed when gently heated with acids according to the scheme:



Thus, under the same conditions, deoxyxanthine, deoxyheteroxanthine, and deoxyparaxanthine form 5-aminomethyl-4-iminazolones and evolve carbon dioxide, with similar velocities. On the other hand, 3-methylxanthine, theobromine, theophylline, and caffeine are much more stable towards acids, and when hydrolysed undergo more complicated reactions, which do not yield definite products. It is suggested that the ready and simple hydrolysis depends on the possibility of the deoxyxanthine reacting in the tautomeric form



Tables are given showing the results of determinations of the rate of hydrolysis of deoxyxanthine, deoxyheteroxanthine, and deoxyparaxanthine, as measured by the carbon dioxide evolved and by the ammonia formed. The 5-aminomethyl-4-iminazolones, formed by the acid hydrolysis of the deoxyxanthines, are strongly basic, amorphous substances, readily soluble in water, and are unstable, but form stable, crystalline salts.

5-Aminomethyl-1-methyl-4-iminazolone, from deoxyheteroxanthine, is isolated as the *hydrochloride*, $\text{C}_8\text{H}_9\text{ON}_3 \cdot \text{HCl}$, which crystallises in needles, decolorises bromine water, and gives an odour of isonitrile when heated with chloroform and alcoholic potassium hydroxide. The *platinichloride*, $(\text{C}_8\text{H}_9\text{ON}_3)_2\text{H}_2\text{PtCl}_6$, yellowish-red needles; the *picrate*, $\text{C}_8\text{H}_9\text{O}_5\text{N}_5$, yellow needles. *5-Aminomethyl-4-iminazolone hydrochloride*, $\text{C}_8\text{H}_9\text{ON}_3 \cdot \text{HCl}$, from deoxyxanthine, and *5-methylaminomethyl-1-methyl-4-iminazolone hydrochloride*, $\text{C}_9\text{H}_{11}\text{ON}_3 \cdot \text{HCl}$, from deoxyparaxanthine, were analysed.

The hydrolysis of the deoxyxanthines by baryta also has been studied and compared with that of the xanthines. From Fischer's results (Abstr., 1899, i, 262), it was to be expected that the rate of hydrolysis would be related directly to the acidity of the xanthine (Wood, Trans., 1906, 89, 1839). The results now obtained with xanthine, 3-methylxanthine, heteroxanthine, theophylline, paraxanthine, theobromine, and caffeine, and with the corresponding deoxy-compounds, show that this is not the case with either class of substance. Moreover, the rule that the ease of hydrolysis increases with the number of methyl groups, to which the behaviour of the xanthines approximates, does not hold good for the deoxyxanthines.

G. Y.

Brominations by means of Diazobenzene Perbromides. CARL BÉLOW and HERMANN SCHMACHTENBERG (*Ber.*, 1908, 41, 2607—2614).—When diazobenzene perbromide is dissolved in well-cooled acetone or acetophenone and the temperature allowed to rise, a vigorous reaction begins at 14°; hydrogen bromide is evolved, crystals of diazobenzene bromide separate, and a monobromo-derivative of the ketone is formed. When the perbromide is kept for some four to five days, decomposition occurs, phenol and tribromophenol being formed according to the equation: $3\text{PhN}_2\text{Br}_2 + 3\text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_5\text{Br}_3 + \text{OH} + 2\text{PhOH} + 6\text{HBr} + 3\text{N}_2$. Unsaturated compounds can also be converted into dibromides by the action of an acetic acid solution of the per-

bromide. Cinnamic acid, ethyl cinnamate, and phenylpropionic acid have been brominated in this manner.

Acetyl-*p*-aminodiazobenzene perbromide (Silberrad and Smart, *Trans.*, 1906, 89, 170) is much more stable than diazobenzene perbromide, and gives up bromine only when kept for several weeks in a moist atmosphere. The corresponding acetyl-*p*-aminodiazobenzene bromide, $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{Br}$, is also stable, m. p. 116°. It may be kept in a desiccator over calcium chloride; it is readily soluble in water, and is very slowly decomposed by water at the ordinary temperature. The perbromide of the acetyl derivative also acts as a brominating agent. J. J. S.

Hydrolysis of Vignin. THOMAS B. OSBORNE and FREDERICK W. HEYL (*Amer. J. Physiol.*, 1908, 22, 362—372).—Vignin is the name given to the principal protein of the seeds of the cow-pea (*Vigna sinensis*); it is a globulin freely soluble in a 5% solution of sodium chloride, and nearly insoluble in a 1% solution of the same salt. The yield of cleavage products brought about by acid hydrolysis was: glycine, 0; alanine, 0.97; valine, 0.34; leucine, 7.82; proline, 5.25; phenylalanine, 5.27; aspartic acid, 3.97; glutamic acid, 16.89; serine, 0; oxyproline, 0; tyrosine, 2.26; cystine, not determined; arginine, 7.2; histidine, 3.08; lysine, 4.28; ammonia, 2.32; tryptophan, present; total, 59.65%. W. D. H.

Constitution of Nucleo-proteins. The Constituents of Pepsin. LOUIS HUGOUNENQ and ALBERT MOREL (*Compt. rend.*, 1908, 147, 212—214).—Crude pepsin extracted from the gastric mucous membrane of the pig by 4 parts of 0.2% hydrochloric acid at 50° yielded on hydrolysis by concentrated acids: tyrosine, 1.7%; alanine, 3.2%; valine, 7.5%; leucine, 11.4%; phenylalanine, 2.2%; lysine, 6.5%; arginine, 2.0%; adenine, 0.5%; xanthine, less than 0.01%; guanine, 0.2%; glucosamine, 1.4%; ψ -histidine, 0.4%, and ψ -lysines, 0.5%. The last-named substances are new; ψ -histidine, $\text{C}_4\text{H}_8\text{O}_2\text{N}_2$, is a diamino-acid, precipitable by silver nitrate, which was analysed as such and as the benzoyl derivative; the ψ -lysines are two substances yielding picrates which remain dissolved in the mother liquor of lysine picrate. One of the new picrates melts at 216°, and belongs to a substance, $\text{C}_{11}\text{H}_{24}\text{O}_5\text{N}_3$, which appears to be a dipeptide derived from lysine and glutamic acid. G. B.

Identity of Nucleic Acids of Thymus, Spleen, and Pancreas. WALTER JONES (*J. Biol. Chem.*, 1908, 5, 1—26).—It is pointed out that many of the differences which have been described in various nucleic acids are due to the difficulties in estimating their cleavage products, to different methods employed, and to admixture with guanylic acids. The three nucleic acids investigated in this research appear to be identical, the special points worked out being specific rotation under varying conditions, and the degree of viscosity of the sodium salts. The so-called gelatinous sodium salt and the non-gelatinous salt are readily convertible one into the other, and this

offers a simple explanation of the physiological localisation and migration of nucleic acid. W. D. H.

Adsorption of Ferments. LEONOR MICHAELIS (*Biochem. Zeitsch.*, 1908, 12, 26—27. Compare this vol., i, 587).—By using more dilute solutions of pepsin, it is found that it is adsorbed by kaolin in acid or alkaline media. It is uncertain how much of this may not be due to mechanical adsorption. W. D. H.

Enzyme Action. XII. The Enzymes of Emulsin. HENRY E. ARMSTRONG, E. FRANKLAND ARMSTRONG, and EDWARD HORTON (*Proc. Roy. Soc.*, 1908, 80, B, 321—331).—The enzyme solutions were prepared for the purposes of the experiments directly from almonds. The extract at 15° exerted but little action on lactose, whereas β -methylglucoside underwent hydrolysis to a considerable extent; at 30° both substances were hydrolysed rapidly. On heating the extract at 45° for three hours, it lost its power of hydrolysing milk-sugar; it retained its activity as a hydrolyst of β -methylglucoside, amygdalin, and salicin, not only after twenty hours' heating at 45°, but also when heated for several hours at 55°. The enzyme was destroyed at about 59°. Other experiments were carried out with the object of effecting a separation of different enzymes by macerating almonds at different temperatures; by macerating with water at 0°, for example, and then macerating the extracted paste with a further quantity of water at 45°, two preparations of emulsins were obtained; both hydrolysed lactose at 38°; only that made at the lower temperature, however, produced any perceptible hydrolysis at 15°, indicating that the gluco-lactase had been preferentially extracted at 15°. The rate of hydrolysis of milk-sugar by extracts of almonds was investigated both without addition of, and in the presence of, added dextrose and galactose. The former alone caused considerable inhibition. The evidence obtained indicates the existence of a lactase in almonds, distinct from emulsin proper (β -glucase). Investigations were also made on the rate of hydrolysis of amygdalin, both the hydrocyanic acid and dextrose being estimated during the course of hydrolysis by special methods, which are described. The amount of Fischer's glucoside separated from partly hydrolysed material was always small; apparently there is no great difference in the rate at which this glucoside and amygdalin are hydrolysed by the β -glucase. S. B. S.

Action of Acids on the Coagulation of Milk by Vegetable Rennets. C. GERBER (*Compt. rend.*, 1908, 146, 1111—1114).—It is shown that with vegetable ferments which coagulate boiled milk more readily than fresh milk, the addition of small quantities of citric, succinic, butyric, phosphoric, or hydrochloric acids retards the action of the rennet, whilst larger quantities accelerate it. In the case of rennets which curdle fresh milk more quickly than boiled milk, all the above acids, with the exception of citric acid, have an accelerating action; citric acid has a retarding effect, except when present in small quantity (compare *Abstr.*, 1907, i, 1100). W. P. S.

Influence of Certain Iron Compounds and of Peroxydases on the Catalysis of Hydriodic Acid by Hydrogen Peroxide. JULES WOLFF and E. DE STOEKLIN (*Compt. rend.*, 1908, 146, 1415—1417. Compare this vol., i, 490; ii, 573).—Colloidal ferrous ferrocyanide behaves as a peroxydase in most cases, but does not activate the decomposition of hydriodic acid by hydrogen peroxide. The latter activation is, however, brought about by ferric thiocyanate and by most peroxydases, but in the case of the ferments it appears to be due to the admixture of a specific enzyme, since particularly pure and potent peroxydases have been prepared which had but a feeble effect on the reaction between hydriodic acid and hydrogen peroxide.

G. B.

A Graphic Method for Registering Certain Fermentation Processes. CARLO FOÀ (*Biochem. Zeitsch.*, 1908, 11, 382—399).—An apparatus is described for graphically registering oxidative processes taking place in the presence of oxydases. The substances under investigation are placed in one vessel, which is connected with a second vessel containing water, with a layer of oil on the surface to prevent oxidation. The two vessels are immersed in a constant-temperature bath, and can be filled with either air or oxygen. The second flask is connected with a Mosso plethysmograph. The apparatus is so arranged that, as the oxygen is used up in the process, water flows back from the plethysmograph into the second vessel; the amount which flows back can be automatically registered by means of a feather pointer on a blackened surface. A special thermo-regulator was constructed for maintaining constant temperatures, as the Ostwald thermostat was not sufficiently sensitive. The carbon dioxide evolved during the oxidative processes was also investigated. S. B. S.

Purification of Peroxydase. ALEXIS BACH and JACOB TSCHERNIAK (*Ber.*, 1908, 41, 2345—2349).—Peroxydase, prepared by the Bach-Chodat method (*Abstr.*, 1903, i, 377), always contains large amounts of carbohydrates and gum-like substances, and activates comparatively small amounts of hydrogen peroxide. Attempts to purify the peroxydase by alternate solution in water and precipitation by means of alcohol have been unsuccessful (this vol., i, 238). A more active peroxydase has now been obtained by treating the expressed juice of turnips with basic lead acetate, removing the excess of lead by means of sodium carbonate, dialysing the solution through a parchment membrane, and finally precipitating the peroxydase by means of alcohol. The peroxydase thus obtained forms a greyish-white powder, contains 7.87% of water, 81.66% of organic matter, 1.47% of ash, and 3.44% of nitrogen calculated for the ash-free substance, and has the activation coefficient, 22.7. As Stocklin's purified peroxydase, containing 11.41% water, 65.88% organic matter, 22.71% ash, and 3.43% nitrogen, had the activation coefficient 2, the activity of the peroxydase is evidently not related to its percentage of nitrogen or of ash. The new peroxydase gives the biuret and xanthoprotein reactions, but not Millon's reaction, and when heated evolves pyrrole and a strongly alkaline base. It renders hydrogen peroxide active towards the oxida-

tion of phenols and aromatic bases, as also towards that of hydrogen iodide. These observations are in agreement with Bach's view (Abstr., 1907, i, 268, 810) that peroxidase is a single enzyme. Whilst when heated in the water-bath the purified peroxidase is destroyed completely only in eighteen minutes, if diluted with 20 vols. of water, it is destroyed under the same conditions in three minutes. G. Y.

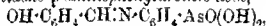
Occurrence of Formaldehyde in Cell-free Fermentation.

ALEXANDER LEBEDEF (Biochem. Zeitsch., 1908, 10, 454—457).—In cases of fermentation by yeast juice in Walton's shaking apparatus, after the fermentation was over, and shaking was continued day and night, a reverse action occurred, and some of the carbon dioxide was absorbed. No proof, however, could be obtained that sugar was formed anew, but formaldehyde was found. W. D. H.

Preparation of Derivatives of *p*-Aminophenylarsinic Acid.

KURATORIUM DER GEORG AND FRANJISKA SPEYER'SCHEN STUDIENSTIFTUNG (D.R.-P. 193543).—*p*-Aminophenylarsinic acid condenses readily with aldehydes to furnish azomethine derivatives.

p-Hydroxybenzylidene-*p*-aminophenylarsinic acid,



obtained by melting its components together at 140—150° and crystallising the product from alcohol, is a sparingly soluble, yellow powder, which is hydrolysed by boiling water, the components again condensing as the aqueous solution is cooled. Similar products are described from *p*-dimethylaminobenzaldehyde and resorcyaldehyde. G. T. M.

Secondary Aromatic Arsinic Acids.

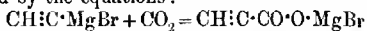
LOUIS BENDA (Ber., 1908, 41, 2367—2373).—Michaelis prepared dinitrodiphenylarsinic acid (Abstr., 1902, i, 515) from diphenylchloroarsine, but was unable to obtain the corresponding diamino acid by reduction. Such diamino-diarylsarinic acids, $\text{As}(\text{R}\cdot\text{NH}_2)_2\cdot\text{O}\cdot\text{OH}$, have now been prepared by heating aromatic amines with arsenic acid at 170—180° (compare Bechamp, Compt. rend., 1863, 56, 1172). These diamino-acids resemble aminophenylarsinic acid in their general behaviour, having both acid and basic properties, but do not form precipitates with magnesia mixture, are soluble in alcoholic sodium hydroxide, and, when diazotised and coupled with β -naphthylamine, form dyes which are insoluble in alkalis. Unmordanted vegetable fibres have only a small affinity for the dye formed by coupling diazotised di-*p*-aminodiphenylarsinic acid with 6-amino-1-naphthol-3-sulphonic acid. When diazotised and boiled, the diamino-diarylsarinic acids yield the corresponding dihydroxy-acids, $\text{As}(\text{R}\cdot\text{OH})_2\cdot\text{O}\cdot\text{OH}$.

Di-*p*-aminodiphenylarsinic acid, $\text{C}_{12}\text{H}_{13}\text{O}_2\text{N}_2\text{As}$, formed together with *p*-aminophenylarsinic acid by heating arsenic acid with aniline at 180—200°, crystallises in needles, m. p. 233°, and forms a white precipitate with silver nitrate in neutral solution. The diacetyl derivative, $\text{C}_{16}\text{H}_{17}\text{O}_4\text{N}_2\text{As}$, forms amber-coloured prisms, m. p. 263°. Di-*p*-hydroxydiphenylarsinic acid, $\text{C}_{12}\text{H}_{11}\text{O}_4\text{As}$, crystallises in plates, m. p. 233°.

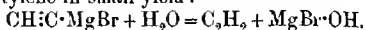
Di-*p*-aminodi-*o*-tolylarsinic acid, $\text{C}_{14}\text{H}_{17}\text{O}_2\text{N}_2\text{As}$, crystallises in

prisms, m. p. 243° . The *diacetyl* derivative, $C_{18}H_{21}O_4N_2As$, forms glistening prisms, m. p. 237° , decomp. 255° . *Di-p hydroxy-o-toyl-arsinic acid*, $C_{14}H_{15}O_4As$, has m. p. 247° .
G. Y.

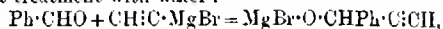
Magnesian-acetylene Bromide. II. BERNARDO ODDO (*Gazzetta*, 1908, 38, i, 625—635. Compare Abstr., 1904, i, 862).—When magnesian-acetylene bromide is treated successively with carbon dioxide and dilute sulphuric acid, a small amount of propiolic acid is formed, the reactions being expressed by the equations:



and $2CH_3C \cdot CO \cdot O \cdot MgBr + H_2O + H_2SO_4 = MgSO_4 + MgBr_2 + H_2O + 2CH_3C \cdot CO_2H$. The interaction of magnesian-acetylene bromide and water gives acetylene in small yield:



The hydrocarbon, m. p. 213 — 214° , which is obtained by the action of benzaldehyde on magnesian-acetylene bromide, to which the formula $C_{18}H_{14}$ was ascribed (*loc. cit.*), is shown to be *s*-tetraphenylethane, m. p. 209° . The formation of this compound and of the others mentioned (*loc. cit.*) is due to the interaction of benzaldehyde and magnesium phenyl bromide which has remained uncharged during the action of the acetylene. Phenylacetylene-carbinol is formed in small quantity by the action of benzaldehyde on magnesian-acetylene bromide and subsequent treatment with water:



which with H_2O gives $OH \cdot CHPh \cdot C \cdot CH_3$.

T. H. P.

Organic Chemistry.

Formal Types of Structural Isomerides. CONRAD LAAR (*J. pr. Chem.*, 1908, [ii], 78, 165—200).—An attempt to classify the different types of structural isomerides.

The main groupings are :

(I). Didesmic forms or isomerides with two changes of linking, for instance, $\text{CH}_3\cdot\text{CHBr}\cdot\text{CH}_3$ and $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$.

(II). Tridesmic forms or isomerides with three changes of linking, such as *o*-nitrophenol and *o*-quinoneoxime.

(III). Tetradesmic forms or isomerides with four changes of linking, for instance, *p*-nitrosophenol and *p*-quinoneoxime.

Each of these main groups is divided into sub-groups: (a) Isomerism without change of valency; (b) isomerism with change of valency, and each sub-group is split up into a number of smaller divisions.

J. J. S.

Some Physical Properties of Butane and *iso*Butane. PAUL LEBEAU (*Bull. Acad. roy. Belg.*, 1908, 300—304).—The author has re-determined the boiling points and some other physical constants of butane and *isobutane* on specimens of the pure hydrocarbons obtained by the action of metalammonium compounds on the corresponding alkyl halide (Abstr., 1905, i, 401).

n-Butane, prepared by the action of sodammonium on *n*- or *sec.* butyl iodide, solidifies in liquid air, has b. p. $0\cdot3^\circ/755$ mm., and a critical temperature $151\text{--}152^\circ$; *isobutane*, obtained by the action of sodammonium or calcium-ammonium on *isobutyl* chloride, is also solid in liquid air, has b. p. $-10\cdot5^\circ/757$ mm. [Noyes, this vol., i, 305, finds b. p. $-11\cdot5^\circ/760$ mm.], and a critical temperature $134\text{--}135^\circ$. The solubilities of the two hydrocarbons in various solvents have also been determined, and the results are comprised in the following table :

	Pressure in millimetres of mercury.	Temperature.	Volume of gas dissolved in one volume of solvent.	
			Butane.	<i>iso</i> Butane.
Water	772	17°	0·15	0·13
Alcohol	775	17	15·83	13·2
Ether	778	18	29·8	27·9
Chloroform	768	17	32·5	39·5

M. A. W.

Molecular Weight of Hexacontane. KARL STRUVE (*Annalen*, 1908, 362, 123—124).—Hexacontane was prepared by Hell and Hagele (Abstr., 1889, 575) by acting on myricyl iodide with potassium. These authors did not, however, determine the mol. wt. of the compound, and, since it might possibly be an unsaturated hydrocarbon,

$C_{20}H_{40}$, the mol. wt. has been determined by Landsberger's boiling-point method. The values obtained agree with the formula $C_{20}H_{40}$.
W. H. G.

Reciprocal Transformation of Isomerides under the Influence of Chemical Induction. SEBASTIAN M. TANATAR (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 806—810).—It was discovered by Skup (Abstr., 1891, 1338) that one exothermic reaction may induce another reaction, also exothermic, a phenomenon to which this author gave the name consonance. Thus, when hydrogen sulphide and sulphur dioxide react together in a medium containing maleic acid, the latter is transformed into fumaric acid.

The author gives further instances of this phenomenon. The transformation of cyclopropane into propylene is induced by the reaction $2NO + O_2 = N_2O_4$ at the ordinary temperature, but the interaction of hydrogen sulphide and sulphur dioxide has no such effect; so that not all exothermic reactions are able to induce isomeric change, the conditions necessary in any particular case being unknown.
T. H. P.

Action of Sulphur on Acetylene. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1908, 305).—Two years ago the author observed that thiophen is not formed by the action of acetylene on fused sulphur in the absence of air, and he is therefore able to confirm the results obtained by Capelle (this vol. i, 201).

M. A. W.

Preparation of Acetylene Di- and Tetra-chlorides from Acetylene and Antimony Pentachloride. HARRY K. TOMPKINS (D.R.P. 196324).—Acetylene di- and tetra-chlorides (*s*-dichloroethylene and *s*-tetrachloroethane) may be prepared by passing the required amounts of acetylene into antimony pentachloride, or a mixture of this chloride with antimony trichloride, and then distilling the product, which contains probably an additive compound of acetylene and the pentachloride.
G. T. M.

Decomposition of Chloroform by Alcoholic Alkali Hydroxides. GUSTAV MOSSLER (*Monatsh.*, 1908, 29, 573—581).—The decomposition of chloroform by alcoholic potassium hydroxide yields carbon monoxide, formic acid, and ethylene, the latter hitherto undetected. Contrary to the general belief, carbon monoxide is the main product: only in favourable circumstances is as much as half of the chloroform converted into formic acid. In the first two series of experiments, 20%, 5%, and 1% solutions of potassium hydroxide in absolute or in 50% alcohol are added to known amounts of chloroform. In all cases a constant volume ratio, 75:25, exists between the amounts of carbon monoxide and ethylene. The same ratio is attained in the third series of experiments, in which an alcohol-chloroform mixture is dropped on to powdered potassium hydroxide, provided that the molecular proportion of alcohol to chloroform exceeds 5:1.

The decomposition of chloral by alcoholic potassium hydroxide also

leads to the formation of carbon monoxide and ethylene in the ratio 3:1 by volume.

The formation of these two gases is explained by the decomposition of the chloroform into hydrogen chloride and carbon dichloride, CCl_2 , the transitory existence of which is indicated by the formation of carbonyl chloride in an experiment in which air and chloroform vapour are passed over a layer of potassium hydroxide. The production of formic acid is due to direct hydrolysis of the chloroform. *

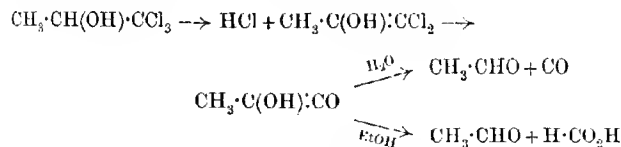
The decomposition of bromoform by alcoholic potassium hydroxide, in which, apart from potassium bromide, only carbon monoxide and ethylene in the ratio 3:1 are produced, is similarly explained by the total conversion of the bromoform into hydrogen bromide and carbon dibromide. The constant ratio of carbon monoxide to ethylene is explained by the action of the carbon dichloride on the alcohol, whereby the esters $\text{CCl}(\text{OEt})$ and $\text{C}(\text{OEt})_2$ are formed in the proportion of 1:2; the latter is directly hydrolysed, and the former decomposes into carbon monoxide and ethyl chloride, which is then converted by the alkali into ethylene. C. S.

Decomposition of Trichloroisopropyl Alcohol by Aqueous or Alcoholic Alkali Hydroxides. GUSTAV MOSSLER (*Monatsh.*, 1908, 29, 583—590. Compare preceding abstract).—The organic products of the decomposition of *aaa*-trichloroisopropyl alcohol by 5–20% aqueous potassium hydroxide are mainly carbon monoxide and acetaldehyde, together with small amounts of formic and lactic acids.

When 5% alcoholic potassium hydroxide (6 mols.) reacts with the alcohol (1 mol.), the chief products are acetaldehyde and formic acid, lactic acid being formed only in small amount; no gas is evolved unless the mixture is warmed, when a relatively small amount of carbon monoxide is liberated.

In no case could the intermediate formation of chloroform be detected.

The author's explanation is indicated in the scheme :



with the intermediate formation of ethyl formate.

C. S.

Composition of the Vapour from Mixtures of Ethyl Alcohol and Water. H. MASING (*Chem. Zeit.*, 1908, 32, 745).—With the object of verifying Gröhning's tables, a careful study of the composition of the alcohol vapour has been made, and it is found that the original values given by him are all too high; those given by Sorel are too low. The influence of pressure and the presence of

impurities such as acetaldehyde, ethyl acetate, and amyl alcohol on the volatility has also been observed.

J. V. E.

Preparation of Difluoroethyl Alcohol. FRÉDÉRIC SWARTS (*Bull. Acad. roy. Belg.*, 1908, 272-282).—In earlier papers (Abstr., 1903, i, 222, 725) the author has described the preparation of difluoroethyl alcohol by the action of metallic oxides and water on difluoroethyl bromide, and has shown that the best results are obtained with mercuric or lead oxide at 160°, but in no case is a theoretical yield obtained.

A repetition of the experiments, using large quantities (1400 grams) of difluoroethyl bromide, shows that when mercuric oxide is the hydrolytic agent, the yield of the alcohol is 93% of that required by theory, the 7% loss being due to a secondary reaction, yielding difluoroacetic acid (Abstr., 1903, i, 727) and mercurous bromide. When lead oxide replaces mercuric oxide, the yield of the alcohol amounts to 92% of that required by theory, the loss being again due to secondary reactions resulting in the formation of glycollic and oxalic acids, together with metallic lead. In this case, the lead oxide first hydrolyses the difluoroethyl alcohol to glycolaldehyde, which in its turn reduces the lead oxide, forming glycollic acid and metallic lead, and part of the glycollic acid undergoes a further oxidation, yielding oxalic acid.

M. A. W.

Methylation in the Ethylene Derivatives from the Point of View of Volatility. LOUIS HENRY (*Compt. rend.*, 1908, 147, 405-408).—The normal effect of the replacement of hydrogen combined with carbon in organic compounds by the methyl group is to raise the boiling point. This is the case even with the monatomic aliphatic alcohols. Substitution of hydrogen by methyl in the glycols, however, has the reverse effect, thus: $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ has b. p. 197-198°; $\text{OH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{OH}$, b. p. 188°; $\text{OH}\cdot\text{CHMe}\cdot\text{CHMe}\cdot\text{OH}$, b. p. 184°; $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{OH}$, b. p. 178°; $\text{OH}\cdot\text{CMe}_2\cdot\text{CHMe}\cdot\text{OH}$, b. p. 178°, and $\text{OH}\cdot\text{CMe}_2\cdot\text{CMe}_2\cdot\text{OH}$, b. p. 174°, although in the case of the corresponding hydrocarbons the b. p. rises regularly, thus: $\text{CH}_3\cdot\text{CH}_3$, b. p. -102°; $\text{CHMe}\cdot\text{CH}_3$, b. p. -50°; $\text{CMe}_2\cdot\text{CH}_3$, b. p. -6°; $\text{CHMe}\cdot\text{CHMe}$, b. p. 1-2°; $\text{CMe}_2\cdot\text{CHMe}$, b. p. 36°; $\text{CMe}_2\cdot\text{CMe}_2$, b. p. 73°. The explanation of this difference lies in the fact that the hydrocarbons are unimolecular, whilst their hydroxyl derivatives are associated in the liquid state.

The decreasing rise in boiling point as the hydrogen of methyl alcohol is replaced by methyl shows that the degree of association is thereby lowered, the elevation of the boiling point by increase in molecular weight being more and more counteracted by the decrease in molecular complexity. The progressive fall in the boiling points of the glycols indicates that here the latter effect is greater than the former.

The dichlorohydrins and the ethylene oxides derived from the above hydrocarbons correspond with the latter in volatility; thus the compounds resulting when the double linking in the above five hydrocarbons is

saturated by chlorine (2 atoms) or by oxygen (1 atom) have their boiling points in the same order as those of the parent compounds. It is deduced that the oxides, as well as the chlorohydrins, are uni-molecular or very slightly associated.

E. H.

Use of Magnesium in place of Zinc in the Synthesis of Alcohols of the Allyl Series. W. JAVORSKY (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 782—787).—Several authors have attempted to replace by magnesium the zinc employed in the synthesis of alcohols of the allyl series from an allyl haloid and a carbonyl compound, but with unsatisfactory results. The author finds, however, that this synthesis takes place readily if the reacting compounds in molecular proportions are allowed to act on magnesium (1 atom) in anhydrous ether. In this way, he has obtained good yields of (1) dimethylallylcarbinol from a mixture of allyl chloride and bromide with acetone; (2) phenyl-methylallylcarbinol from allyl iodide or bromide and acetophenone; (3) diphenylallylcarbinol from allyl bromide and benzophenone; (4) methylpropylallylcarbinol from allyl bromide and methyl propyl ketone.

Also, ω -bromostyrene reacts readily in ethereal solution with magnesium, yielding styrene and diphenylvinylethylene. If the magnesium compound formed is treated with carbon dioxide, cinnamic acid, as well as diphenylvinylethylene, is formed. The reaction between magnesium and ω -bromostyrene hence proceeds in two directions: (1) the removal of the halogen from 2 molecules of the bromostyrene by the magnesium; (2) normally, giving an organo-magnesium compound, which, on decomposition with water, yields styrene and with carbon dioxide gives cinnamic acid.

T. H. P.

Contact Oxidation of Ethyl Ether. E. I. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 799—800).—When oxidised by the contact process, ethyl ether yields acetaldehyde and a small proportion of formaldehyde: $\text{Et}_2\text{O} + \text{O}_2 = 2\text{C}_2\text{H}_4\text{O} + \text{H}_2\text{O}$; $\text{Et}_2\text{O} = 2\text{C}_2\text{H}_4 + \text{H}_2\text{O}$; $\text{C}_2\text{H}_5 + \text{O}_2 = 2\text{CH}_3\text{O}$. The gaseous products consist of carbon dioxide (7.55%), oxygen (2.11%), carbon monoxide (5.33%), hydrogen (1.86%), nitrogen (78.25%), and ethylene (2.9%).

T. H. P.

Pressure and Composition of the Vapours of Aqueous Solutions of the Ether of Ethylene Glycol. A. E. MAKOVETSKI (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 752—760).—The author makes use of the following dynamical method, which allows of the simultaneous and accurate determination of the pressure and composition of the vapour from a mixture of two volatile liquids.

In a small thermostat filled with water at the room temperature is a flask containing air and provided with a manometer. By means of a known weight of water, a known volume of air, V , at pressure p mm., and saturated with water vapour having the pressure h at t , is driven out of the flask, through a calcium chloride tube, and then through a nine-bulbed Will and Bredig apparatus placed in a thermostat and containing the solution to be investigated; in all the author's experiments, this second thermostat was maintained at $50 \pm 0.05^\circ$. The

vapour-laden air then passes through a spiral condenser immersed in solid carbon dioxide, and deposits its vapour quantitatively. The spiral is subsequently dipped into alcohol and into ether to remove traces of oil and water, and is then weighed, the increase in weight giving the amount of vapour in the volume V of air.

For determining the proportions of the ether of ethylene glycol and water in the condensed liquid, the author made use of the refractive index, which had been previously measured for a number of aqueous solutions of the ether.

Knowing the composition of the vapour, the number of milligram-mols. of each of the components in a weighed quantity of the condensed liquid can be calculated, and from the sum, a , of the numbers of milligram-mols. for the two components, the vapour pressure of the solution in mm. of mercury can be found by means of the equation: $H = B [V(B + p - h)/22.4 \cdot a \cdot 760(1 + \alpha t) + 1]$, where B is the atmospheric pressure, t the temperature of the thermostat containing the flask filled with air, and H the sum of the partial pressures of the two components of the vapour.

A solution containing 56.5 mols. % of the ether of ethylene glycol has the maximum vapour pressure, and boils unchanged. The specific heat and D of this solution are considerably higher than the calculated values.

For the pure ether, the mean specific heat at 16–100° is 0.4365–0.4377, and the heat of evaporation at atmospheric pressure, 89.95–90.08 Cals. per gram. Trouton's constant is hence 21.2, which shows that in the liquid condition the ether is not associated, although the lowering of the partial pressure of water by the vapour is twice as small as it should be according to Raoult's law. T. H. P.

Studies in Steam Distillation. Formic and Acetic Acids. H. DROOP RICHMOND (*Analyst*, 1908, 33, 305–312).—The results of experiments on the rate of distillation of aqueous solutions of formic and acetic acids are given, the apparatus employed being specially designed to prevent condensation in the head of the retort. The rate of distillation of the acids relatively to that of water is given, together with the results calculated from the formulae given previously (this vol., i, 495). W. P. S.

Spectroscopic Reaction for Oleic Acid. ISAAC LIFSCHITZ (*Zeitsch. physiol. Chem.*, 1908, 56, 446–452).—The characteristic reaction given by oleic acid (this vol., i, 263) is best shown when an acetic acid solution of chromic acid is used as the oxidising agent. To a mixture of 1 drop of oleic acid in 3–4 c.c. of glacial acetic acid and 1 drop of a 10% solution of chromic acid, also in glacial acetic acid, 10 drops of concentrated sulphuric acid are added. After a short time, a violet to cherry-red coloration develops, and ultimately becomes so deep that dilution with acetic acid is necessary before the characteristic absorption bands can be observed. Oleoglycerides give the same reaction, but the addition of chloroform is advisable.

The sensitiveness is 1 in 10,000 to 1 in 15,000.

Trichloroacetic acid produces the same coloration as the acetic

and sulphuric acids. These reactions for oleic acid and cholesterol are thus practically identical. J. J. S.

Formation of γ -Lactones. ALEXIS A. SHUKOFF and PETER J. SCHESTAKOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 830—839).—The authors have investigated the conditions of transformation of oleic acid into lactone, and also the extent to which other unsaturated ethylenic acids with the double linking not in the γ -position are able to undergo this transformation. It has been found that saturated alcohol-acids also yield lactones, the hydroxyl group wandering to the γ -position, giving a γ -hydroxy-acid and subsequently a γ -lactone. The best method of converting the acids into lactones is to heat them with anhydrous zinc chloride or concentrated sulphuric acid. When treated in this way, oleic, elaidic, isooleic, θ -hydroxystearic, and ϵ -hydroxystearic acids all yield γ -stearolactone, erucic acid yields γ -behenolactone, and $\kappa\lambda$ -undecylic acid, γ -undecolactone. Crotonic and α -hydroxybutyric acids, however, give no lactone. Indeed, under these conditions, lactones are only given by those ethylenic acids and saturated hydroxy-acids in which the double linking or hydroxyl group is at least four carbon atoms away from the carboxyl group.

It is probable that the oleic acid separated from fats is not a chemical individual, but consists of a mixture of isomerides having double linkings, not only in the θ -position, but also in the $\beta\gamma$ - or $\gamma\delta$ -position. To see whether it is the latter alone which yields lactone, the θ -acid was prepared from ϵ -hydroxystearic acid, and was found to give about 10% of γ -stearolactone when treated with zinc chloride. γ -Stearolactone, obtained in 35% yield by the action of concentrated sulphuric acid on commercial oleic acid (compare Abstr., 1904, i, 646), has an iodine number 16—20 and a mean molecular weight, assuming it to be a monobasic acid, 375, which, after boiling with alcoholic potassium hydroxide, falls to 291. This indicates that the lactone contains a considerable proportion of a compound with the character of an anhydride or complex ether, analogous to those formed on heating hydroxystearic acid. After distillation, the iodine number and, consequently, the proportion of unsaturated compound increase considerably, indicating the presence of hydroxystearic acids, which are converted into unsaturated acids on distillation. If the pure stearolactone is treated with sulphuric acid, it is partly converted into soluble, acid products, which contain sulphur and are probably sulphonic-acids. Conversion of part of the stearolactone into these sulpho-compounds probably determines, to some extent, the small yield of the lactone.

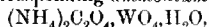
γ -Behenolactone, $\text{CH}_3 \cdot [\text{CH}_2]_{16} \cdot \text{CH} < \begin{smallmatrix} \text{O} \\ \text{CO} \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix}$, crystallises from light petroleum in shining plates, m. p. 63.5° , and, on oxidation with chromic acid, yields γ -ketobehenic acid, $\text{C}_{22}\text{H}_{42}\text{O}_3$, forming colourless crystals, m. p. 103° .

γ -Undecolactone, $\text{C}_{11}\text{H}_{20}\text{O}_2$, b. p. 286° , is converted into γ -hydroxyundecic acid, m. p. 34° , by acids or alkalis. T. H. P.

Complex Ozo-salts of Tungsten. ARRIGO MAZZUCHELLI and GIUSEPPE INGHILLERI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 30—33. Compare Abstr., 1907, i, 748).—The tendency of tungsten to form ozo-

salts is not so marked as that exhibited by its higher analogue, uranium, or by molybdenum, and the ozo-salts are readily soluble and difficult to obtain free from the normal salts used in their preparation. On this account no lithium ozotungsten oxalate could be isolated, whilst the potassium and barium salts were only obtained in an impure condition.

Sodium ozotungsten oxalate, $\text{Na}_2\text{C}_2\text{O}_4 \cdot \text{WO}_4 \cdot 5\text{H}_2\text{O}$, obtained by the action of hydrogen peroxide on the compound $\text{Na}_2\text{C}_2\text{O}_4 \cdot \text{WO}_3$, forms white crystals. The corresponding *ammonium salt*,



forms white, sphaero-crystals; the *calcium salt*, $\text{CaC}_2\text{O}_4 \cdot \text{WO}_4 \cdot \text{H}_2\text{O}$, was also prepared.

T. H. P.

Esterification of Malonic Acid. ISAAC K. PHELPS and E. W. TILLOTSON, jun. (*Amer. J. Sci.*, 1908, [iv], 26, 243—252).—In earlier papers (Abstr., 1907, i, 823; this vol., i, 166), methods have been described for obtaining good yields of ethyl succinate and benzoate. A study has now been made of the best conditions for the esterification of malonic acid. The largest yield, 96.1%, was obtained by heating an alcoholic solution of malonic acid with sulphuric acid at 50° for eight hours, and treating the residue with a fresh quantity of alcohol for two hours.

E. G.

Purification of Esters. ISAAC K. PHELPS, M. A. PHELPS, and E. A. EDDY (*Amer. J. Sci.*, 1908, [iv], 26, 253—256).—A study has been made of the purification of ethyl succinate, malonate and benzoate, containing alcohol, water, unchanged organic acid, and small quantities of mineral acid. It has been found that these esters may be purified without much loss by heating them in suitable conditions with dry potassium carbonate under reduced pressure. A comparison of this method with that of extracting the ester with ether has shown that the loss by the former method is rather greater in the case of ethyl benzoate, but is smaller in the cases of ethyl succinate and malonate. The potassium carbonate method, however, is to be preferred even with ethyl benzoate, since it affords greater ease of manipulation and is less expensive. The smaller the quantity of free acid present, the more completely can the ester be recovered.

E. G.

Conversion of Ethyl Cyanoacetate into Ethyl Malonate ISAAC K. PHELPS and E. W. TILLOTSON, jun. (*Amer. J. Sci.*, 1908, [iv], 26, 257—263).—The conditions under which ethyl cyanoacetate is converted into ethyl malonate have been carefully investigated. It was found that when a well-cooled mixture of 50 grams of ethylcyanoacetate, 125 c.c. of absolute alcohol, and 4 grams of sulphuric acid was saturated with hydrogen chloride by passing in a stream of the dry gas for four hours, and the product heated for two hours at 100—110° with 200 c.c. of absolute alcohol, a yield of 96.3% of ethyl malonate was obtained.

E. G.

Influence of Catalytic Agents in Ester Formation. Esterification of Cyanoacetic Acid. ISAAC K. PHELPS and E. W. TILLOTSON, jun. (*Amer. J. Sci.*, 1908, [iv], 26, 264—266).—The effects

produced on the esterification of cyanoacetic acid by varying the proportions of the reagents, the catalysers, and the time of reaction have been studied. The results show that by the use of alcohol alone, a yield of 63% of the ester can be obtained, but that the yield is increased by the presence of a catalytic agent, and within certain limits by the amount of the catalyst employed. The esterification is rendered more complete by increasing the time of reaction. Alcoholic hydrogen chloride causes the formation of some ethyl malonate, but this change does not occur when sulphuric acid is employed. Nearly theoretical yields of ethyl cyanoacetate can be obtained by heating 50 grams of cyanoacetic acid with 2 grams of sulphuric acid and 200 c.c. of absolute alcohol for two hours at 100–110°. E. G.

Preparation of Malonic Acid or its Ester from Monochloroacetic Acid. ISAAC K. PHELPS and E. W. TILLOTSON, jun. (*Amer. J. Sci.*, 1908, [iv], 26, 267–274).—In earlier papers (preceding abstracts) an account has been given of the best conditions for the esterification of malonic acid and for the conversion of ethyl cyanoacetate into ethyl malonate. A further study has now been made with special reference to the preparation of ethyl malonate from chloroacetic acid.

It has been found that the reaction between potassium cyanide and sodium chloroacetate to form sodium cyanoacetate proceeds best in alkaline solution, and takes place vigorously at 110°, or slowly at 90–95°, without affecting the yield of ethyl malonate. The alkaline solution of sodium cyanoacetate should not be evaporated to dryness at a high temperature, or even be boiled for a long time, since these conditions favour the formation and subsequent decomposition of sodium malonate. After acidifying the solution of sodium cyanoacetate with sulphuric acid and removing the precipitated salt by filtration, the resulting solution of cyanoacetic acid is concentrated under reduced pressure at 70–80°. The precipitated salt is washed with alcohol, and the alcoholic solution is evaporated at about 60°. The residues, consisting of cyanoacetic acid and some of its ester and sodium salt, are converted into ethyl malonate by the method described previously (*loc. cit.*). By this means a yield of 92% of ethyl malonate can be obtained.

The ester can be converted into pure malonic acid by heating it with an equal quantity of water and a few drops of nitric acid at about 60° for some time after the mixture has become homogeneous, and evaporating the solution to the point of saturation. The malonic acid which separates on cooling is recrystallised from hot water. E. G.

Preparation of Cyanoacetic Acid and its Ester from Monochloroacetic Acid. ISAAC K. PHELPS and E. W. TILLOTSON, jun. (*Amer. J. Sci.*, 1908, [iv], 26, 275–280).—Sodium chloroacetate and potassium cyanide react quantitatively in alkaline solution to form sodium cyanoacetate. A study has now been made of the formation of ethyl cyanoacetate from monochloroacetic acid, the method of esterification of cyanoacetic acid being that described previously (preceding abstract). The results show that ethyl cyanoacetate can be obtained in

good yield if precautions are taken to minimise the transformation into malonic acid. Pure cyanoacetic acid can be prepared by heating a mixture of two parts of water with one part of the ester and a few drops of nitric acid at about 60° for some time after the mixture has become homogeneous. The solution is then evaporated at $50-60^{\circ}$ to the point of saturation, and the cyanoacetic acid which separates on cooling is recrystallised from a mixture of ether and chloroform.

E. G.

Saponification of Fats by means of Hydroxylamine. EUGENIO MORELLI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 74-76).—In order to obtain derivatives of fats which crystallise well and have melting points higher than those of the acids from which they are derived, the author has studied the action of hydroxylamine on fats. The hydroxamic acids obtained are very stable, and fulfil the above conditions.

Stearohydroxamic acid, $C_{17}H_{35}\cdot C(OH):NOH$, prepared from tri-stearin and hydroxylamine, separates from alcohol in crystals, m. p. 104° , and in alcoholic solution gives a reddish-violet colour with ferric chloride.

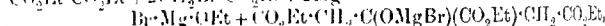
Palmitohydroxamic acid, $C_{15}H_{31}\cdot C(OH):NOH$, which is deposited from alcohol in crystals, m. p. 99° , and *oleohydroxamic acid*,

$C_{17}H_{33}\cdot C(OH):NOH$, m. p. 61° , both give the red colour with ferric chloride in alcoholic solution. The latter is resolved into oleic acid and hydroxylamine sulphate when boiled with dilute sulphuric acid.

A mixture of stearohydroxamic and palmitohydroxamic acids has m. p. 95° ; the lowering of m. p. here observed can doubtless serve to establish the proportions of the two acids in a mixture of them.

T. H. P.

New Synthesis of Citric Acid. ENOS FERRARIO (*Gazzetta*, 1908, 38, ii, 99-100).—By the condensation of ethyl bromoacetate with diethyl oxalate in presence of magnesium according to the equation:



$Br \cdot Mg \cdot OEt + CO_2Et \cdot CH_2 \cdot C(OMgBr)(CO_2Et) \cdot CH_2 \cdot CO_2Et$, the author obtains a compound which, when treated with dilute sulphuric acid, yields an oil, b. p. $215^{\circ}/35$ mm., and appears to be triethyl citrate. The reaction is being studied further. T. H. P.

Structure of Glucinum Salts. SEBASTIAN M. TANATAR and E. K. KUROVSKI (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 787-790. Compare Abstr., 1907, i, 888; this vol., i, 166, 502).—The following salts of glucinum have been prepared:

With tricarballic acid, the salt, $Gl_3(C_6H_5O_6)_2$, obtained as a white powder insoluble in all the ordinary solvents.

With citric acid, the salt, $\left[\begin{array}{c} O-Gl-O-CO \\ | \\ Gl \cdot CO \cdot O \cdot CH_2 \end{array} \right]_2 C(OH) \cdot CH_2 \cdot CO_2 \Big]_2 Gl$, which is of a more basic type, $Gl_2O_2X_2$, than most of the glucinum salts, Gl_4OX_6 .

With salicylic acid, glucinum forms the salt, $(OH \cdot C_6H_4 \cdot CO_2Gl \cdot O)_2Gl$,

with phthalic acid, the salt, $C_6H_4 \begin{smallmatrix} \diagup CO_2Gl \cdot CO_2 \cdot C_6H_4 \cdot CO_2Gl \cdot O \\ \diagdown CO_2Gl \cdot CO_2 \cdot C_6H_4 \cdot CO_2Gl \cdot O \end{smallmatrix} Gl$, and with lactic acid, the salt, $(OH \cdot CHMe \cdot CO_2Gl \cdot O)_2Gl$.

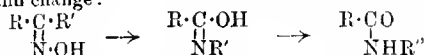
In addition to the benzoate already described (this vol., i, 166), glucinum yields a *benzoate* of the normal type, $Gl_4O(C_7H_5O_2)_6$, which is obtained on prolonged boiling of a solution of benzoic acid in a mixture of equal volumes of alcohol and benzene with glucinum carbonate; this salt has the molecular weight 710 (theor. 779) in freezing benzene.

The interaction of sodium benzoate and a glucinum salt in aqueous solution yields various salts, which are more or less basic according to the concentrations, temperatures, and acidities of the solutions, and are insoluble in organic solvents. T. H. P.

Isomerism of Ethyl Acetoacetate. R. H. MCCREA (*Chem. News*, 1908, 98, 127).—The enolic form of ethyl acetoacetate may, like other unsaturated compounds, be represented as having a *trans*- (I) and a *cis*- (II) configuration:



The *cis*-configuration (II) must be unstable, as it corresponds with the hypothetical intermediate product in Bernthsen's representation of the Beckmann change:



and must therefore change at once into the ketonic form of the ester. The action of phosphorus pentachloride leads, now, to the formation of β -chloroerotic acid, $\begin{array}{c} Me \cdot C \cdot Cl \\ | \\ H \cdot C \cdot CO_2H \end{array}$ or $\begin{array}{c} Me \cdot C \cdot Cl \\ | \\ CO_2H \cdot C \cdot H \end{array}$. This acid should be stable, as it cannot undergo the second stage of the Beckmann change; in agreement with this view is its conversion into *isocrotonic* acid, which is considered to be the stereoisomeride of *crotonic* acid. It cannot be decided which of the modifications, the stable or the unstable, has the *cis*-configuration, as either configuration might be the unstable form. It is suggested that *isocrotonic* acid has the form

$\begin{array}{c} Me \cdot C \cdot OH \\ | \\ CO_2H \cdot C \cdot H \end{array}$, as it is formed from the chloro-acid, which also forms

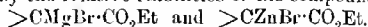
tetrollic acid, $\begin{array}{c} Me \cdot C \\ | \\ CO_2H \cdot C \end{array} + \begin{array}{c} Cl \\ | \\ H \end{array}$, and may therefore be considered to have the hydrogen and chlorine atoms spatially near each other, $\begin{array}{c} Me \cdot C \cdot Cl \\ | \\ CO_2H \cdot C \cdot H \end{array}$ G. Y.

Action of Magnesium on Esters of Brominated Fatty Acids. **New Synthesis of Ketonic Esters.** JOSEF ZELTNER (*J. pr. Chem.*, 1908, [ii], 78, 97—123. Compare this vol., i, 243).—In the ordinary Reformatzky synthesis of hydroxy-acids, the zinc cannot be replaced by magnesium. When magnesium is used, at least three reactions take place: (1) Reduction of the brominated ester to the corresponding

fatty ester; (2) formation of a β -ketonic ester; (3) production of a high boiling, crystalline compound. The yield of ketonic ester is best when an *isobromo-ester* is used, for example:

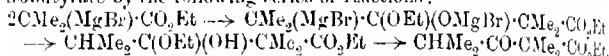
Ethyl bromopropionate	gives 85.3 per cent.	ethyl propionylpropionate.
Ethyl bromobutyrate	„ 40.5 „	ethyl butyrylbutyrate.
Ethyl bromoisobutyrate	„ 67.3 „	ethyl isobutyryldimethylacetate.
Ethyl bromoisovalerate	„ 60.3 „	ethyl valerylvalerate.

The difference in the reactions with zinc and magnesium is accounted for by the relative stabilities of the compounds



By the action of *p*-tolaldehyde on the product of the interaction of magnesium and ethyl α -bromoisobutyrate, a small amount of a crystalline substance, $\text{C}_{16}\text{H}_{20}\text{O}_3$, m. p. 138—139°, is obtained.

Ethyl isobutyryldimethylacetate, $\text{CHMe}_2\cdot\text{CO}\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et}$, has b. p. 202.5—203°/745.5 mm., and, when boiled with aqueous potassium hydroxide, yields diisopropyl ketone. It is formed from ethyl α -bromoisobutyrate by the following series of reactions:



Ethyl butyrylbutyrate has b. p. 222.8—223.4°/755 mm. (compare Hamonet, Abstr., 1890, 235).

Ethyl isovalerylisovalerate, $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}(\text{CHMe}_2)\cdot\text{CO}_2\text{Et}$, obtained from ethyl α -bromoisovalerate, has b. p. 237.2—237.4°/768 mm. (corr.), and, on hydrolysis, yields isovalerone.

Ethyl bromoacetate does not give ethyl acetoacetate (compare Stollé, this vol., i, 310).

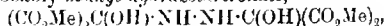
J. J. S.

Methyl Mesoxalate and Some of its Reactions. RICHARD S. CURTISS and PAUL T. TARROWSKI (*J. Amer. Chem. Soc.*, 1908, 80, 1264—1271).—In an earlier paper (Curtiss, Abstr., 1906, i, 480), a method was described for the preparation of ethyl mesoxalate by the action of nitrogen trioxide on ethyl malonate by which a yield of 90—95% could be obtained.

It has now been found that a yield of 80—85% of methyl mesoxalate can be obtained in a similar manner. The mother liquor obtained in this reaction yields a light green mixture of unstable, oily esters, which are of an acid nature and contain nitrogen. This product decomposes suddenly at 120—130°, and yields yellow potassium, ammonium, and silver salts.

When methyl mesoxalate is distilled under reduced pressure, methyl oxomalonate, $\text{CO}(\text{CO}_2\text{Me})_2$, b. p. 100°(uncorr.)/20 mm., is obtained. Pure anhydrous methyl oxomalonate has been prepared, and its reactions are being studied.

By the action of hydrazino carbonate on methyl mesoxalate, a compound, probably *methyl hydrazotartrons*,



m. p. 154—155°, is obtained, which forms white crystals. If this substance is mixed with phosphoric oxide, it is converted into a yellow, crystalline compound, which is probably an azimethylene derivative. When the hydrazo-compound is treated with benz-

aldehyde, benzylideneazine (Curtius and Jay, Abstr., 1889, 393) is produced.
E. G.

Conversion of Methyl Alcohol into Formaldehyde and Preparation of Formalin. IV. E. I. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1903, 40, 796—799. Compare this vol., i, 77).—The author gives further details for carrying out this oxidation. Platinised pumice and platinised asbestos act as good catalysts. By using these, the preliminary heating in a furnace of the tubes containing copper gauze may be dispensed with. The proportion of acetone in the methyl alcohol should not exceed 2%. When 4% of acetone is present, the contact mass does not ignite, and with 2.5% ignition takes place when the temperature is 34—35° and the current of air amounts to 3 litres per minute; only when the greater part of the acetone has burnt away does the copper gauze begin to ignite.

T. H. P.

Condensation Products of Acetaldehyde containing Six and Ten Atoms of Carbon. SIMON ZEISEL and BÉLA VON BITTÓ (*Monatsh.*, 1903, 29, 591—605).—Ten volumes of acetaldehyde are heated for thirty-six hours at 95—97° with 1 volume of saturated sodium acetate solution, and the product distilled in steam. The distillate is fractionated, and, after removal of crotonaldehyde, the portion boiling above 120° purified by repeated distillation in steam, shaking with calcium carbonate, and drying, is separated by fractional distillation into two substances, both having the composition C_6H_8O and exhibiting the properties of an aldehyde with two ethylenic linkings; the one has b. p. 75—80°/24—26 mm., yields an impure oxime, m. p. 155.5°, and an unstable, crystalline phenylhydrazone, whilst the other has b. p. 55—60°/24—26 mm. and 141—143° under ordinary pressure, forms an unstable oxime and phenylhydrazone, and yields, by oxidation with free oxygen, formic acid and resinous and other unexamined products.

From the residue of the original preparation non-volatile in steam, a substance, $C_{10}H_{14}O_2$, b. p. 159—163°/16.5 mm., has been isolated, which contains one $ClIO$ group (the other oxygen atom being probably in the form of a "bridge"), does not form a definite oxime or phenylhydrazone, and reacts with bromine, evolving hydrogen bromide.

C. S.

Crystalline Polymeride of isoButaldol. R. MUSSELIUS (*J. Russ. Phys. Chem. Soc.*, 1903, 40, 822—826).—The author has subjected to further investigation the crystalline substance, m. p. 90—92°, isolated by Brauchbar (Abstr., 1897, i, 137) from the condensation products of isobutaldehyde, and characterised by him as isobutaldol. By repeated fractional crystallisation from benzene, the compound is obtained in bundles of slender, white needles, m. p. 96.5—97°. In freezing benzene, the molecular weight corresponds with the formula $(C_4H_{10}O_2)_n$, a result in accordance with those of Kohn (Abstr., 1900, i, 274) for other crystalline aldols, which were all found to be bimolecular polymerides of the liquid aldols. In freezing acetic acid,

the molecular weight is 300—309.5 (theory, 288), but ebullioscopic measurements in ether gave unsatisfactory results, probably owing to decomposition of the double molecules of the aldol.

T. H. P.

Preparation of Ketone ortho-Ethers. EDGAR HESS (D.R.P. 197804).—Nitriles of the general formula $R \cdot CN$ are converted into the hydrochlorides of imino-esters by treatment with hydrogen chloride in absolute alcohol, and the product mixed with a ketone in the same medium. After eight days' shaking, the ammonium chloride produced is precipitated by ether, the filtrate poured into ice water, and the ketone ortho-ether separated from any ester by fractional distillation. The following acetals were thus produced: From methyl ethyl ketone, $CMeEt \cdot C(OEt)_2$, b. p. $68^\circ/10$ mm., $120^\circ/760$ mm.; from diethyl ketone, $CEt_2 \cdot C(OEt)_2$, b. p. $71^\circ/44$ mm., $154^\circ/760$ mm., and from dipropyl ketone, $CPr_2 \cdot C(OEt)_2$, b. p. $69^\circ/12$ mm.

G. T. M.

Action of Ammonia on Methyl Ethyl Ketone. CARL THOMAE (*Arch. Pharm.*, 1908, 246, 373—377).—The use of alcohol as a solvent in this reaction, described by Traube (this vol., i, 362), was introduced by the author (*Abstr.*, 1905, i, 509).

G. B.

Solubility and Certain Reactions of Pinacolin. LÉON DELANGE (*Bull. Soc. chim.*, 1908, [iv], 3, 910—915).—The author finds that, contrary to Denigès' statement (*Abstr.*, 1903, i, 606), pinacolin does not form an additive compound with mercuric sulphate, but that the precipitate obtained with ordinary samples of pinacolin is due to the presence of impurities which are not entirely removed by fractionation. In order to prepare pure pinacolin, the ordinary product is rectified seven times with a Le Bel column, warmed with mercuric sulphate, and the filtrate again warmed with the reagent. After decanting, the pinacolin is dried, washed, and rectified (b. p. 106.2°). Pure pinacolin dissolves in water to the extent of 2.44% at 15° , and its solubility at 15° in aqueous acetone is (by volume) 1 part in 28.8 parts of 20° , 1 in 16.5 of 33° , 1 in 11.0 of 50° , and 1 in 7.0 of 60° . When 1 c.c. of pinacolin is added to a mixture of 0.45 c.c. of acetone and 1.8 c.c. of water, 0.30 c.c. of acetone is absorbed by the water and 0.15 c.c. by the pinacolin, and in a mixture of 1.65 c.c. of acetone and 0.85 c.c. of water, 0.75 c.c. of acetone is absorbed by the water and 0.60 c.c. by the pinacolin. The author shows that acetone can be estimated in presence of pinacolin by precipitation with mercuric sulphate. Pure pinacolin gives Legal's colour reaction (*Abstr.*, 1897, ii, 467), as stated by Denigès, but it does not furnish iodoform when treated with iodine and potassium hydroxide; the precipitate obtained is soluble in acetic acid, and has m. p. 68° , and at the same time there is formed a small amount of a volatile liquid of a piquant odour.

J. C. C.

Action of Hydroxylamine on Ketones of the Type $CHR:CH \cdot CHECH \cdot CO \cdot R$.

ROBERTO CIUSA and A. TERNI (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 724—728. Compare *Abstr.*, 1907, i, 62).—In addition to the compounds α -cinnamylideneacetophenonehydroxylamine and α -cinnamyl-

ideneacetophenoneoxime previously isolated as products of the action of hydroxylamine on cinnamylideneacetophenone, isomeric forms of these substances can also be separated in small quantities. These are denoted as β -forms, and their properties are compared with those of the α -compounds.

α -Cinnamylideneacetophenoneoxime (m. p. 135°) gives a benzoyl derivative crystallising from alcohol in white needles, m. p. 125°. β -Cinnamylideneacetophenoneoxime crystallises in white needles, m. p. 139–140°, and gives a benzoyl derivative, m. p. 137°. β -Cinnamylideneacetophenonehydroxylamine forms small, white spangles, m. p. 198°.

Cinnamylideneacetophenone is not toxic in its properties; the α -oxime is more poisonous, but 4–5 grams can be administered per day; so-called resinoid acids are then found in the urine, together with large quantities of uroresin. The latter fact is remarkable, as uroresinuria has not previously been induced by artificial means. α -Cinnamylideneacetophenonehydroxylamine differs from the other substances in being highly poisonous, probably in virtue of the $\cdot\text{NH}\cdot\text{OH}$ group, as in the case of phenylhydroxylamine. W. A. D.

N-Alkylketoximes. JOHANNES SCHEIBER (*Annalen*, 1908, 362, 54–63).—Previous work has shown that *N*-alkylketoximes are produced only with great difficulty by the condensation of β -substituted hydroxylamines with ketones (compare Scheiber and Wolf, *Abstr.*, 1907, i, 1028). In the case of acetone, ethyl acetoacetate, methyl ethyl ketone, and diacetyl, the additive compounds first formed by the reaction with the β -substituted hydroxylamine, namely, *N*-alkylketoxime hydrates, were isolated, but similar substances were not obtained from benzyl methyl diketone or benzil. With the object of ascertaining to what extent various ketones condense with β -benzylhydroxylamine, the following method was devised, by which the isolation of the additive product became unnecessary.

Known weights of β -hydroxylamine and of the ketone are added to a known weight of benzene, and the depression of the freezing point of the solvent noted at once and at intervals of some hours. If no interaction takes place, the depression observed is that calculated from the weights of ketone and β -benzylhydroxylamine added; should the observed depression be smaller than the calculated, then interaction must have taken place. Methyl ethyl diketone is found to react at once, whilst benzil does not react with β -benzylhydroxylamine.

The following ketones interact slowly with β -benzylhydroxylamine, the difference between the observed and calculated depression of the freezing point increasing slowly during several hours: acetone, methyl ethyl ketone, methyl propyl ketone, methyl isopropyl ketone, methyl butyl ketone, benzyl methyl ketone, diethyl ketone, acetophenone, and *m*-nitroacetophenone. It is found that the homologues of acetone do not condense so readily with β -benzylhydroxylamine as acetone itself, with the one exception of benzyl methyl ketone, which apparently interacts more rapidly than acetone. The additive power of the ketone is reduced considerably by replacing a methyl group by ethyl, phenyl, or *m*-nitrophenyl.

The effect on the rate of formation of the additive compounds, produced by the addition of *p*-toluidine, diphenylamine, dimethylaniline, triethylamine, and tribenzylamine, was also investigated.

Generally speaking, the presence of a base does not bring about an acceleration in the rate of condensation; in fact, triethylamine appears to retard the reaction.

W. H. G.

***N*-Alkylketoximes.** JOHANNES SCHEIBER and PAUL BRANDT (*Annalen*, 1908, 362, 64—77).—The work described in the previous paper (compare Scheiber, preceding abstract) has been repeated, and so that the reactivities of the various ketones might be compared, equal molecular solutions have been used in each case. In all cases an experiment was performed in which the molecular proportions of ketone and β -benzylhydroxylamine were as 1:1, and sometimes as 5:1. The results obtained may be summarised as follows:

(1) In the absence of a base, the rate of formation of the additive product decreases rapidly in the following order: benzyl methyl ketone, acetone, methyl butyl ketone (methyl ethyl ketone = methyl hexyl ketone), diethyl ketone, acetophenone. Acetophenone, even in strong solutions, is almost indifferent towards β -benzylhydroxylamine.

(2) In the presence of a base, such as triethylamine, tribenzylamine, or dimethylaniline, the rate at which the additive product is formed is apparently smaller, but it is only apparent, for in some cases the difference between the calculated and observed depression of the freezing point at first increases and then decreases, undoubtedly because the second reaction, *N*-benzylketoxime hydrate \rightarrow *N*-benzylketoxime + water, is taking place. The apparent reduction in the velocity of formation of the *N*-benzylketoxime hydrate is due to the occurrence of this second reaction. In fact, the solution containing β -benzylhydroxylamine, benzyl methyl ketone, and triethylamine, or tribenzylamine, becomes turbid after some time, owing to separation of water.

It is therefore evident that the difference in the behaviour of an aldehyde and a ketone towards β -substituted hydroxylamines is merely one of degree and not of kind.

W. H. G.

The Scission of Sugars. [Sucroclasm.] II. The Action of Zinc Dust and Iron on Formaldehyde Solutions; the Action of Zinc Dust on Dextrose. WALTHER LÖB (*Biochem. Zeitsch.*, 1908, 12, 466—472. Compare this vol., i, 715).—As products of the action of zinc dust on formaldehyde were isolated, formic acid and two other volatile products were obtained in the form of their condensation products with phenylhydrazine. The one gave an insoluble osazone, m. p. 243°, which corresponded in properties with diacetyl-osazone, and the other gave an osazone, m. p. 148°, which is methylglyoxalosazone. The other products of reaction have not yet been all identified. They appear to include β -acrose, as an osazone of m. p. 165° was obtained. Polyhydroxy-acids were also obtained. When formaldehyde solutions are treated with iron, condensation to sugars takes place to only a slight extent, and only traces of polyhydroxy

acids are formed. Methyl alcohol and formic acid are produced, however, in larger quantities. Dextrose, on treatment with zinc, yields formic acid, diacetyl, and methylglyoxal, also polyhydroxy-acids, but no methyl alcohol. S. B. S.

The Depolymerisation of Sugars. CARL NEUBERG (*Biochem. Zeitsch.*, 1908, 12, 337—341).—Pure crystalline glycerose was prepared by the method of Fenton and Jackson, and polymerised by treating with a colloidal solution of barium carbonate in methyl alcohol. By this means a pentose was obtained, as furfuraldehyde could be obtained by distillation of the condensation product with hydrochloric acid, and was isolated in the form of its condensation product with *p*-nitrophenylhydrazine. As pure glycerose was employed, the formation of a pentose from the triose can only be explained by assuming that the latter depolymerises to formaldehyde, an assumption that is rendered probable by the work of Buchner and other investigators. S. B. S.

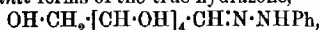
Preparation of an Anhydrous Crystalline Compound of Dextrose and Sodium Iodide. FUNIA JOHANN A. WÜLFING (D.R.P. 196605).—The compound $2C_6H_{12}O_6 \cdot NaI$, octahedral crystals, m. p. 185—186°, is produced by boiling together anhydrous dextrose and sodium iodide in alcoholic solution; it separates on diluting the solution with about 10% of water and allowing to cool. G. T. M.

Phenylhydrazones of Dextrose. ROBERT BEHREND and FRIEDRICH LOHR (*Annalen*, 1908, 362, 78—114).—The compound, m. p. 106—107°, obtained by the action of an alcoholic solution of phenylhydrazine on dextrose, either in the solid state or in strong aqueous solution, and described previously (Abstr., 1907, i, 481) as being identical with Skraup's β -phenylhydrazone, is now shown to be a loose combination of 1 mol. of phenylhydrazine with 2 mols. of a hydrazone, which it is proposed to call dextrose- β -phenylhydrazone. Skraup's β -hydrazone is merely a mixture of this hydrazone with some α -hydrazone. Another compound, containing 1 mol. of phenylhydrazine loosely combined with 1 mol. of the β -hydrazone, has also been isolated. A solution of either of the hydrazones or phenylhydrazine additive compounds in hot pyridine deposits on cooling a pyridine additive compound of the β -hydrazone, from which the pure β -hydrazone is obtained by washing with cold alcohol. It is thus possible to pass from the α - to the β -isomeride.

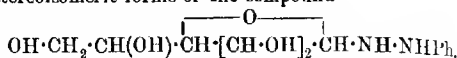
Solutions of either the α - or β -hydrazone in pyridine, having the approximate initial values $[\alpha]_D - 87^\circ$ and -10° respectively, become dextrorotatory when kept for some time. If these solutions are heated at 80—85° for about one and a-half hours and then cooled rapidly, the value observed in each case is roughly $[\alpha]_D + 18.5^\circ$; the rotation gradually decreases at the ordinary temperature, the final value being roughly $[\alpha]_D + 5^\circ$. All attempts to separate the dextrorotatory isomeride present in these solutions were unsuccessful.

The possible structural formulæ of the isomeric phenylhydrazones

are discussed. It is considered probable that the α - and β -hydrazones are the *syn*- and *anti*-forms of the true hydrazone,



or that one of them is a true hydrazone; whilst the other is one of the possible stereoisomeric forms of the compound



The velocity with which one isomeride passes into the other in solution is increased by traces of acid and diminished by alkalis. The equilibrium mixture of the two hydrazones in aqueous solution has the optical rotatory power $[\alpha]_D^{20} = -53.74^\circ$.

The substance, $(\text{C}_6\text{H}_{12}\text{O}_5\cdot\text{N}\cdot\text{NHPh})_2\cdot\text{NHPh}\cdot\text{NH}_2$, previously described as dextrose- β -phenylhydrazone (*loc. cit.*), is best prepared by the action of phenylhydrazine on dextrose in dilute aqueous alcoholic solution; traces of ammonia retard the formation of this substance to a great extent. The same compound is also formed by the action of an alcoholic solution of phenylhydrazine on either solid α - or β -dextrose. An aqueous solution (2–4%) ten minutes after dissolving the substance gave $[\alpha]_D = -4.4^\circ$, the final value being $[\alpha]_D = -48.2^\circ$.

The substance, $\text{C}_6\text{H}_{12}\text{O}_5\cdot\text{N}\cdot\text{NHPh}\cdot\text{NHPh}\cdot\text{NH}_2$, prepared by the action of phenylhydrazine (3 parts) on dextrose (1 part), crystallises in concentric groups of large, white prisms, which sinter at about 80° , m. p. $85\text{--}87^\circ$; a 4% aqueous solution ten minutes after dissolving the substance gave $[\alpha]_D = -2.82^\circ$, the final value being $[\alpha]_D = -23.45^\circ$.

The change in the optical rotatory power of an alcoholic solution with the time is very remarkable; a solution of 0.5017 gram in 25 c.c. gave the following values: $[\alpha]_D +3.24^\circ$, $\pm 0.00^\circ$, -3.49° , -4.98° , $\pm 0.00^\circ$, $+2.49^\circ$, -7.97° , -14.95° at 20, 30, 70, 90 minutes, 4.5, 21.5, 46.5, and 94 hours respectively.

The pyridine additive compound of dextrose- β -phenylhydrazone, $\text{C}_6\text{H}_{12}\text{O}_5\cdot\text{N}\cdot\text{NHPh}\cdot\text{C}_5\text{NH}_5$, crystallises in small, colourless, trapezoidal plates, m. p. $100\text{--}101^\circ$. In aqueous solution, the initial value is $[\alpha]_D = -4.08^\circ$, the value after several hours being -38.87° .

Dextrose β -phenylhydrazone, $\text{C}_6\text{H}_{12}\text{O}_5\cdot\text{N}\cdot\text{NHPh}$, is best prepared by treating the pyridine additive compound with small quantities of alcohol. It may also be obtained in the same way from the phenylhydrazine compound, m. p. 107° . It crystallises in small needles, m. p. $140\text{--}141^\circ$; the optical rotation of an aqueous solution containing a trace of pyridine twenty minutes after dissolution was $[\alpha]_D = -5.50^\circ$, the equilibrium value being $[\alpha]_D = -53.74^\circ$. The α -hydrazone crystallises from a solution of the β -hydrazone in alcohol containing a small amount of acetic acid at about 20° ; the substance, m. p. $106\text{--}107^\circ$, which separates from the same solution at 0° , and was previously thought to be the β -hydrazone, is a mixture of the two isomerides. The β -hydrazone may be obtained from the α -isomeride by boiling an alcoholic solution of the latter for some time and then rapidly cooling to 0° .

W. H. C.

The Precipitation of Sugars by Cupric Hydroxide. S. YOSHIMORO (*Zeitsch. physiol. Chem.*, 1908, 56, 425–445. Compare Salkowski, this Journ., 1872, 25, 1122; Worm-Müller and Hagen, *Pflüger's Archiv*, 1876, 17, 568).—Experiments have been made by

precipitating cupric hydroxide (from cupric sulphate solution by the addition of sodium hydroxide) in the presence of various sugars. Even when excess of alkali is used, small amounts of sugar are found in the filtrates.

The amount of sugar, however, tends to decrease if the mixture is shaken thoroughly and kept for some little time before filtration.

In the case of all the sugars examined, the amount of sugar left in the filtrate decreases as the amount of alkali is increased, but this value reaches a minimum, and further addition of alkali tends to increase the amount of sugar in the filtrate. With lactose, xylose, and arabinose, the curves are fairly regular, but with dextrose, laevulose, galactose, maltose, sucrose, and raffinose the curves are irregular. In no case is the amount of sugar present in the filtrate directly proportional to the excess of alkali. The minimum has the smallest value in the case of dextrose, namely, 1.66%.

J. J. S.

The Molecular Weight of Dextrin from Honey from Coniferous Plants. HERMANN BARSCHALL (*Chem. Zentr.*, 1908, ii, 91; from *Arbb. Kais. Gesundh.-Amt.*, 1908, 28, 405—419).—The molecular weight of this substance was determined by the cryoscopic method, although it was not found possible to obtain a honey-dextrin free from ash. After the necessary correction for ash has been made, it is found that the value obtained (473) is well above that required for a disaccharide, $(C_6H_{10}O_5)_2 = 324.16$, and falls within the limits of experimental error for a trisaccharide (486.32).

J. V. E.

Action of Nitric Acid on Starch. II. ANTONY G. DOROSCHEWSKY, ADAM W. RAKOWSKY, and A. A. BARDT (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 932—940. Compare *Abstr.*, 1907, i, 678).—In continuation of their previous work, the authors have studied the hydrolysis, by means of 0.4*N* nitric acid, (1) of starch in 8.6% and 14% concentrations, and (2) of starches derived from potatoes, maize, rice, Bermuda arrowroot, and St. Vincent arrowroot.

The results show that in reactions with intermediate stages of the first order, the velocity constant, calculated from the formula for unimolecular reactions, increases slightly as the concentration of the reacting compounds increases. Further, if in these reactions the velocity of the latter stage is much less than that of the first stage, the velocity constant given by the unimolecular formula increases for some time and then remains constant. In particular, a constant velocity-coefficient is obtained when some intermediate stage is taken as the beginning of the reaction.

The velocity constants for the final stage of the hydrolysis of the various starches are: potato, 0.0097; maize, 0.0097; rice, 0.0094; Bermuda arrowroot, 0.0100; St. Vincent arrowroot, 0.0103. The initial stages of the course of hydrolysis vary considerably with the different starches investigated, which may be divided into two groups: (1) rice and maize starches, with which the hydrolysis at first increases,

reaching a maximum in about ten minutes; (2) potato and the two arrowroot starches, with which no such increase is observed.

T. H. P.

Action of Nitric Acid on Cellulose. CARL HÄUSSERMANN (*Chem. Zentr.*, 1908, i, 2024; from *Zeitsch. Schiess. Sprengstoffwesen*, 1908, 3, 121—132).—With nitric acid, cellulose yields additive as well as substitution products. Cotton immersed in cold nitric acid, D 1.1—1.45, then pressed, and allowed to dry for three or four days over lime in a vacuum, as described by Knecht (*Abstr.*, 1904, i, 293), gives additive products. This is shown by the fact that cold water removes the acid, and also the bluish-black coloration produced with iodine-potassium iodide solution. When left in the nitric acid, cotton becomes disintegrated, giving soluble substances, amongst which there is scarcely any nitrate. Left in contact with nitric acid of D above 1.45 for a sufficient length of time, cellulose is converted into the nitrate, which is stable towards water, and when free from acid gives no coloration with iodine-potassium iodide solution.

When cellulose fibre is saturated with excess of concentrated acid and the liquid removed before the action is complete, the product gives a blue coloration with iodine-potassium iodide. Cellulose also gives with stronger nitric acid an additive product, which loses water in presence of excess of acid, forming the ester.

J. V. E.

Influence of Sulphuric Acid in Nitration. Especially of Cellulose. CARL KULLGREN (*Chem. Zentr.*, 1908, i, 2024—2025; from *Zeitsch. Schiess. Sprengstoffwesen*, 1908, 3, 146—149. Compare this vol., i, 504).—The author concludes from the results of Schaposhnikoff, Küster and Kremann, Lunge, and others, that the nitric acid is only capable of nitrating when present as the compound HNO_3 , and not as hydrate; the part played by the added sulphuric acid being to set free HNO_3 from the hydrate.

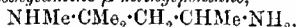
J. V. E.

Two Methods of Preparing Methylamine. MAURICE FRANÇOIS (*Compt. rend.*, 1908, 147, 428—430).—The existing methods of separating ammonia and methylamine are incomplete (compare this vol., i, 505; Bertheaume, this vol., ii, 742). The method of separation by means of yellow mercuric oxide (*Abstr.*, 1907, i, 391) is only applicable to a crude methylamine hydrochloride which contains no other nitrogen base besides ammonia. The crude product obtained in Brochet and Cambier's method (*Abstr.*, 1895, i, 325) of preparing methylamine contains as impurities ammonium chloride, formaldehyde, and trimethyltrimethylenetriamine hydrochloride. The author finds that moderately-concentrated solutions of the latter in hydrochloric acid decolorise a solution of iodine in potassium iodide, afterwards precipitating a brown periodide, and give a pale yellow precipitate with a solution of mercuric iodide in potassium iodide, and that trimethyltrimethylenetriamine hydrochloride is easily soluble in chloroform. By means of these reactions, it is found that Brochet and Cambier's crude hydrochloride, after once recrystallising from alcohol, still contains 3% of the triamine hydrochloride; accordingly, the

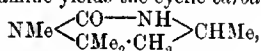
mercuric oxide separation is inapplicable. On the other hand, the crude hydrochloride resulting from Hofmann's reaction with bromoacetamide contains nothing soluble in chloroform (which dissolves the hydrochlorides of secondary and tertiary bases), and treatment by yellow mercuric oxide gives pure methylamine hydrochloride. The conclusion is drawn that Hofmann's reaction, followed by a separation by mercuric oxide, is the more satisfactory method of preparing pure methylamine. The yield, however, is not good; the author obtained 35% of theory, and probably Hofmann's high apparent yield contained ammonium chloride.

E. H.

δ-Amino-β-methylamino-β-methylpentane. MORITZ KOHN and OITO MORGENSTERN (*Monatsh.*, 1908, 29, 519–523).—The oxime of methyl diacetoneamine, when reduced by sodium and absolute alcohol, yields *δ-amino-β-methylamino-β-methylpentane*,



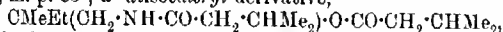
b. p. 166–167°, a mobile, fuming liquid with an intense basic odour; the *aurichloride* and *platinichloride* decompose at 215° and 220° respectively, whilst the *picrate* melts in hot water and decomposes at 199–200°. When heated with 1 mol. of ethyl carbonate for thirty hours at 200°, the diamine yields the cyclic carbamide,



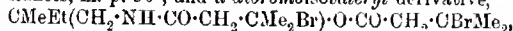
m. p. 132–133°, b. p. 292–293°/741 mm.

C. S.

Preparation of Acylated Aminoalkyl Esters. J. D. RIEDEL (D.R.P. 194051. Compare Abstr., 1906, i, 631; 1907, i, 897).—*Aminodimethylethylcarbinol*, b. p. 75–80°/30 mm., and the secondary base, $\text{NH}(\text{CH}_2 \cdot \text{CMeEt} \cdot \text{OH})_2$, b. p. 145°/30 mm., and *hydrochloride*, m. p. 144°, are obtained by heating, at 125°, chlorodimethylethylcarbinol and aqueous ammonia; the former furnishes a *hydrochloride*, leaflets, m. p. 85°, a *diisovaleryl* derivative,

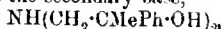


greasy leaflets, m. p. 50°, and a *dibromoisovaleryl* derivative,



needles, m. p. 74°.

Phenylaminodimethylcarbinol, $\text{CMePh}(\text{CH}_2 \cdot \text{NH}_2) \cdot \text{OH}$, b. p. 175°/40 mm., together with the secondary base,



b. p. 258°/40 mm., are obtained by heating, at 125°, phenylchlorodimethylcarbinol and aqueous ammonia; the *dibenzoyl* derivative, prisms, m. p. 110°, is obtained by treating the primary base with benzoyl chloride in pyridine solution.

G. T. M.

Preparation of α-Iodoisovalerylcarbamide. KNOLL & Co. (D.R.P. 197648. Compare Abstr., 1907, i, 1017).—*α-Iodoisovalerylcarbamide*, leaflets, m. p. 180°, is prepared by heating α-chloro- or α-bromo-isovalerylcarbamide with an alkali iodide, or the iodide of an alkaline earth metal, either in alcoholic solution or in the presence of benzene.

G. T. M.

Synthesis of α -Aminonitriles. NICOLAI D. ZELINSKY and GEORGE I. STADNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1906, 40, 790—791).—In the formation of the nitriles of α -amino-acids (Abstr., 1906, i, 425) by the action of potassium cyanide (1 mol.) and ammonium chloride (1 mol.) on aldehydes or ketones, the hydrolysis of the potassium cyanide plays an important part, so that the presence of water is necessary in order that the reaction may take place. That this is the case is shown by experiments with benzaldehyde and with cyclohexanone, which yield no nitrile in the absence of water.

T. H. P.

Preparation of Barium Cyanide from Barium Cyanamides. BADISCHE ANILIN & SODA-FABRIK (D.R.-P. 197394).—The reversible reaction $\text{Ba}(\text{CN})_2 \rightleftharpoons \text{BaCN}_2 + \text{C}$ is applied to the production of barium cyanide. The crude product, containing 60% of cyanide and 40% of barium cyanamide, is heated at 600—800° in a stream of acetylene.

A mixture of barium carbonate and wood-charcoal powder is heated in nitrogen at 1500° until no further absorption of gas is observed. The temperature is then lowered to 1100°, and the mixture treated with a current of producer gas previously freed from carbon dioxide until the product is wholly converted into barium cyanide.

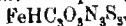
G. T. M.

Mercuric Oxycyanide. ERWIN RUPP and S. GOY (*Arch. Pharm.*, 1908, 246, 367—373. Compare Holdermann, Abstr., 1906, i, 73, 411; Rupp, Abstr., 1906, i, 340).—Mercuric oxide takes part in the formation of the oxycyanide as hydroxide, hence the reaction is accelerated by hydroxyl ions. It is best carried out by mixing 22.2 grams of mercuric oxide in a mortar with 60 c.c. of water and 4 c.c. of 10% sodium hydroxide, adding 27 grams (a slight excess) of mercuric cyanide, and stirring until the mixture is colourless.

Details are also given for the preparation of the oxycyanide from mercuric chloride, mercuric cyanide, and sodium hydroxide, and from alkali cyanide and mercuric chloride. The fact that mercuric salt are not precipitated by sodium hydroxide in the presence of mercuric cyanide depends on the formation of mercuric oxycyanide.

G. B.

Oxidations Effected by Ferric Salts. C. BONGIOVANNI (*Gazzetta*, 1908, 38, ii, 5—9).—The author produces fresh evidence in support of his view concerning the reaction between ferric chloride and potassium thiocyanate (Abstr., 1907, i, 833). According to Tarugi (Abstr., 190 i, 176), the red coloration produced in this reaction is due to the formation of the ferrous salt of a peroxythiocyanic acid,



which, like the free acid, is decolorised by dilution or by solutions of oxalates, tartrates, &c., being converted thereby into normal thiocyanic acid or thiocyanate. The author, however, explains the decoloration produced by dilution as due to the hydrolysis of the non-dissociated red, $\text{Fe}(\text{CNS})_3$, into yellow, colloidal ferric hydroxide and thiocyanic acid; and the decoloration effected by oxalates, tartrates,

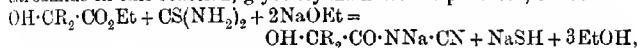
dec. by the formation by these substances of complex ions with the iron of the ferric thiocyanate and consequent displacement of the equilibrium $\text{Fe}^{+++} + 3\text{CNS} \rightleftharpoons \text{Fe}(\text{CNS})_3$ in such a manner that the coloured part is diminished in amount. This view is supported by the observation that the substances which decolorise ferric thiocyanate also hinder the displacement of iodine from potassium iodide by ferric salts.

The author also traverses the statement of Tarugi and Revello (*Atti Soc. Chim. Roma*, July, 1907), that ferric chloride exerts an oxidising action on potassium ferrocyanide, so that the interaction of these compounds results in the formation of ferrous oxyferrocyanide and not of ferric ferrocyanide. By means of a special apparatus, the author has carried out this reaction in an atmosphere of nitrogen, thus avoiding, as far as possible, the formation of soluble Prussian blue. By washing the precipitate, precipitating by sodium hydroxide solution, again washing, and dissolving in acid, always in an atmosphere of nitrogen, a solution is obtained which contains only traces of ferrous salt, attributable to secondary reactions. Tarugi and Revello's interpretation of the reaction is hence erroneous.

T. H. P.

Ureides and Cyanamides of the Dialkylglycollic Acids.

ERIK CLEMMENSEN and ARNOLD H. C. HEITMAN (*Amer. Chem. J.*, 1908, 40, 289—302).—The authors have prepared ureides of the dialkylglycollic acid by substituting one or more of the hydrogen atoms in carbamide by the radicle $\text{OH}\cdot\text{CR}_2\cdot\text{CO}$. By the action of carbamide and sodium ethoxide on the esters of the dialkylglycollic acids, ureides of the formula $\text{OH}\cdot\text{CR}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{CR}_2\cdot\text{OH}$ are obtained, but when thiocarbamide or guanidine (as thiocyanate) is substituted for carbamide in this reaction, glycolcyanamides are produced, thus:



and these cyanamides are converted by boiling with acids or alkalis into the ureides just mentioned. It was found possible, however, to obtain *C-diethylglycollylthiocarbamide*,



by heating a mixture of diethylglycollic acid and thiocarbamide to 180° . At 200° , and with an excess of the latter, $\beta\beta$ -diethylthiohydantoin is formed.

C-Diethylglycollylcarbamide,



forms long, needle-shaped crystals, m. p. $30-31^\circ$. In 100 parts of water, 6.5 parts dissolve at 20° , and 1.4 at 100° . On dry distillation, its salts yield a mixture of diethyl ketone, diethylcarbinol, and probably triethylcarbinol. The calcium, magnesium, copper (normal and acid), zinc, silver, mercury, and double magnesium-copper salts are described.

C-Dipropylglycollylcarbamide forms a white, crystalline mass, m. p. 39° ; the magnesium and mercury salts are described. *C-Dimethylglycollylcarbamide* crystallises from light petroleum in white needles, m. p. 74° . It forms double salts of the formula $\text{C}_{18}\text{H}_{25}\text{O}_{10}\text{N}_4\text{CuR}$ ($\text{R} = \text{Ca, Ba, Sr, or Mg}$); the zinc and silver salts were analysed. *C-Diethyl*

glycollylthiocarbamide separates from water in long, slender, yellow needles or small, rhombic prisms, m. p. 117—118°. β -*Diethylthiohydantoin*, $\begin{matrix} \text{CET}_2\text{-S} \\ \text{CO-NH} \end{matrix} > \text{C:NH}$, separates from water in colourless cubes or octahedrons, m. p. 224°. On boiling with barium hydroxide for an hour, it is converted into *diethylthioglycollamide*, $\text{SH}\cdot\text{CET}_2\cdot\text{CO}\cdot\text{NH}_2$, m. p. 147°, and on prolonged boiling it yields *diethylthioglycollic acid*, $\text{SH}\cdot\text{CET}_2\cdot\text{CO}_2\text{H}$, which is being further examined. *Diethylglycolcyanamide*, $\text{OH}\cdot\text{CET}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CN}$, separates from water in shining plates, m. p. 235°. *Dipropylglycolcyanamide* crystallises from water in colourless, monoclinic needles, m. p. 184°. *Dimethylglycolcyanamide* separates from water in tiny, colourless, monoclinic needles, m. p. 248—250°.

J. C. C.

Resolution of α -Methylisoserine into its Optically Active Components. FRANCIS W. KAY (*Annalen*, 1908, 362, 325—332).— α -Methylisoserine is readily resolved in the form of its benzoyl derivative by means of brucine or quinine.

dl-Benzoyl- α -methylisoserine, $\text{C}_{11}\text{H}_{13}\text{O}_3\text{N}$, prepared by the action of benzoyl chloride and sodium hydroxide on the amino-acid, crystallises in plates, m. p. 153° (corr.). The *brucine* salt of the *d*-compound crystallises from the alcoholic solution of the *dl*-benzoylamino-acid and brucine. *d-Benzoyl- α -methylisoserine*, liberated from its brucine salt by means of sodium hydroxide, crystallises in needles, m. p. 124° (corr.), $[\alpha]_D^{20} + 9.51^\circ$, or, in more dilute solution, $[\alpha]_D^{20} + 8.40^\circ$. *l-Benzoyl- α -methylisoserine*, obtained from the mother liquor of the brucine salts, has $[\alpha]_D^{20} - 9.23^\circ$, or, in more dilute solution, $[\alpha]_D^{20} - 8.39^\circ$, and resembles its optical antipode.

The optically active α -methylisoserines are obtained by hydrolysis of their benzoyl derivatives with boiling hydrobromic acid. The *d*-acid, $\text{C}_7\text{H}_9\text{O}_3\text{N}$, when quickly heated, has m. p. about 230° (decomp.), $[\alpha]_D^{20} + 4.34^\circ$. The *l*-acid has $[\alpha]_D^{20} - 4.15^\circ$, and resembles its optical antipode.

G. Y.

Resolution of α -Amino-*n*-hexoic Acid into its Optical Components. DEMETRIUS MARKO (*Annalen*, 1908, 362, 333—337).— α -Amino-*n*-hexoic acid was resolved previously in the form of its benzoyl derivative (Fischer and Hagenbach, *Abstr.*, 1902, i, 85). It is now found better to employ the formyl derivative.

*dl-Formyl- α -amino-*n*-hexoic acid*, $\text{C}_7\text{H}_{13}\text{O}_3\text{N}$, prepared by Fischer and Warburg's method (*Abstr.*, 1906, i, 72), crystallises in colourless needles, m. p. 113—115° (corr.). On treatment of the *dl*-compound with brucine in alcoholic solution, the *brucine* salt of the *l*-acid separates, and, on hydrolysis by means of hydrochloric acid, yields *l-formyl- α -amino-*n*-hexoic acid*, which crystallises in silky needles, m. p. 115—118.5° (corr.), $[\alpha]_D^{20} - 17.56^\circ$. The *d-formyl* derivative, obtained from the alcoholic mother liquor, has $[\alpha]_D^{20} + 17.63^\circ$.

The formylamino-acids are hydrolysed by boiling 10% hydrobromic acid. *l*- α -Amino-*n*-hexoic acid, $[\alpha]_D^{20} - 22.99^\circ$; the *d*-acid, $[\alpha]_D^{20} + 23.14^\circ$.

Fischer and Hagenbach (*loc. cit.*) obtained the values $[\alpha]_D^{20} - 22.4^\circ$ and $+21.3^\circ$; by a fermentation process, Schulze and Likiernik obtained an acid having $[\alpha]_D - 26.5^\circ$. G. Y.

Synthesis of Polypeptides. XXVI. 1. Derivatives of α -Aminostearic Acid. EMIL FISCHER and WALTER KROPP (*Annalen*, 1908, 362, 338—347).—In comparison with the α -amino-derivatives of the simple fatty acids, the derivatives of the high molecular acids have so far been little studied. As a contribution to the filling of this gap in our knowledge, the authors now describe the combination of glycine with α -aminostearic acid.

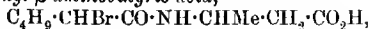
Methyl α -aminostearate hydrochloride, $C_{19}H_{40}O_2NCl$, prepared by treating α -aminostearic acid with methyl alcohol and hydrogen chloride, separates from ethyl acetate in needles, m. p. 112° (corr.). The *hydrochloride* of the ethyl ester crystallises in needles, m. p. 89° (corr.).

Methyl chloroacetylaminostearate, $C_{21}H_{40}O_3NCl$, prepared by the successive action of sodium methoxide and chloroacetyl chloride on the hydrochloride of the preceding methyl ester, crystallises from light petroleum in colourless needles, m. p. 78° (corr.). The *ethyl ester*, prepared in the same manner, crystallises in colourless needles, m. p. 68° (corr.). Hydrolysis of the methyl ester with alcoholic sodium hydroxide leads to the formation of *chloroacetylaminostearic acid*, $C_{20}H_{38}O_3NCl$, which crystallises in colourless needles, m. p. 107° (corr.), and, when heated with alcoholic ammonia at 100° , forms *glycyl- α -aminostearic acid*, $NH_2 \cdot CH_2 \cdot CO \cdot NH \cdot CH(C_{16}H_{33}) \cdot CO_2H$, crystallising in microscopic prisms, m. p. about 218° (corr.). It dissolves in hot dilute hydrochloric acid or sodium hydroxide, forming frothing solutions; concentrated sodium hydroxide precipitates the *sodium salt*.

The *anhydride*, $CH_2 \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{CO} \cdot \text{NH} \end{smallmatrix} \text{CH} \cdot C_{16}H_{33}$, formed by the action of alcoholic ammonia on ethyl chloroacetyl- α -aminostearate at 100° , separates in microscopic crystals, m. p. 219° (corr.), and is insoluble in dilute sodium hydroxide. G. Y.

Synthesis of Polypeptides. XXVI. 2. Derivatives of β -Aminobutyric Acid and of α -Methylisoserine. FRANCIS W. KAY (*Annalen*, 1908, 362, 348—360).—So far only two polypeptides derived from β -amino-acids, leucylisoserine and isoserylisoserine, have been described. As a knowledge of such substances is desirable for the discussion of certain theoretical questions, the author has studied the combinations of *r*- β -aminobutyric acid with *i*-leucine and alanine, and of *r*- α -methylisoserine with *i*-leucine. In the last case both isomeric racemic compounds have been obtained, and are distinguished, as in other similar cases, as the *A* and *B* compounds.

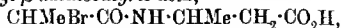
α -Bromoisohexyl- β -aminobutyric acid,



prepared by the action of *i*-bromoisohexoyl chloride and sodium hydroxide on β -aminobutyric acid, crystallises in small prisms or needles, m. p. 97 — 98° ; attempts to resolve it into two forms were unsuccessful. The action of 35% aqueous ammonia on the bromo-compound at 25° leads to the formation of *leucyl- β -aminobutyric acid*,

$\text{NH}_2 \cdot \text{CH}(\text{C}_2\text{H}_5) \cdot \text{CO} \cdot \text{NH} \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, which is obtained as a colourless, crystalline powder, m. p. 232° (corr.). The copper salt, $(\text{C}_{10}\text{H}_{19}\text{O}_2\text{N}_2)_2\text{Cu}_2\text{O}$, forms deep blue, six-sided plates. The anhydride, $\text{C}_{10}\text{H}_{18}\text{O}_2\text{N}_2$, formed by heating the dipeptide at 225° , is obtained as a yellow, sandy powder, m. p. $197-198^\circ$ (corr.), and is probably quadrimolecular.

Bromopropionyl-β-aminobutyric acid,



prepared from β-aminobutyric acid and bromopropionyl bromide, crystallises from water in colourless needles, m. p. 131° (corr.), and, when treated with aqueous ammonia at 25° , yields *alaninyl-β-aminobutyric acid*, $\text{NH}_2 \cdot \text{CHMe} \cdot \text{CO} \cdot \text{NH} \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, which forms an amorphous, slightly grey mass, m. p. about 250° (decomp.), when quickly heated. The copper salt, $(\text{C}_7\text{H}_{13}\text{O}_3\text{N}_2)_2\text{Cu}_2\text{O} \cdot 4\text{H}_2\text{O}$, forms deep blue, six-sided plates.

When coupled with *i*-bromoisohexoyl chloride, α-methylisoserine forms two α-bromoisohexoyl-α-methylisoserines, $\text{C}_{10}\text{H}_{18}\text{O}_2\text{NBr}$. The *A* compound crystallises from the aqueous solution in needles, m. p. 173° (corr.); the *B* compound, obtained from the aqueous mother liquor, crystallises in hexagonal plates, m. p. $125-126^\circ$ (corr.). *Leucyl-α-methylisoserine A*, $\text{NH}_2 \cdot \text{CH}(\text{C}_2\text{H}_5) \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CMe}(\text{OH}) \cdot \text{CO}_2\text{H}$, crystallises in microscopic prisms, m. p. about 240° (decomp.); the phenylcarbimide derivative, $\text{C}_{11}\text{H}_{23}\text{O}_3\text{N}_2$, crystallises in stout prisms, m. p. 180° (corr.). *Leucyl-α-methylisoserine B* crystallises in colourless plates or needles, m. p. 250° (decomp.); the phenylcarbimide derivative forms silky needles, m. p. 187° (corr.). (G. Y.)

Experiments on the Decomposition of Arginine. D. ACKERMANN (*Zeitsch. physiol. Chem.*, 1908, 56, 305-315).—The substance described as putridine (*ibid.*, 54, 24) is now shown to be δ-aminovaleric acid (Salkowski, Abstr., 1898, i, 404). It is thrown down by the reagents usually employed for precipitating alkaloids. When its hydrochloride is heated, it sublimes, and does not yield a ring compound.

Experiments made with the object of proving whether, when arginine undergoes putrefaction, δ-aminovaleric acid is formed, gave negative results. Amongst the products isolated was *r*-ornithine; thus indicating that racemisation had occurred during the reaction. The purification of this base is facilitated by precipitation with mercuric chloride and sodium acetate. Tetramethylenediamine could not be detected.

D-Lysine yields an aurichloride, $\text{C}_{12}\text{H}_{25}\text{O}_4\text{N}_4 \cdot \text{HCl} \cdot 3\text{HAuCl}_4 \cdot 2\text{H}_2\text{O}$, which sinters at 120° and melts at $152-155^\circ$. The aurichloride of the racemic base has the composition $\text{C}_{12}\text{H}_{28}\text{O}_4\text{N}_4 \cdot 4\text{HAuCl}_4 \cdot \text{H}_2\text{O}$, and decomposes at $173-176^\circ$. The corresponding *platinichloride* crystallises with 1 molecule of alcohol, $\text{C}_6\text{H}_{14}\text{O}_2\text{N}_2 \cdot \text{H}_2\text{PtCl}_6 \cdot \text{EtOH}$, which it loses at 120° . (J. J. S.)

Derivatives of a Complex Chloride of Gold and Phosphorus. MARIO LEVI-MALVANO (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 847-857).—The author has prepared the following complex compounds of gold and phosphorus:

Aurophosphorous chloride, $(\text{AuP}\text{Cl}_2)\text{Cl}$ (compare Lindet, Abstr., 1887, 227). Methyl aurophosphite chloride, $[\text{AuP}(\text{OMe})_3]\text{Cl}$ (Lindet, *loc. cit.*), which has the molecular weight 384—425 (calc. 356.65) in freezing benzene, and with chloroplatinic acid solutions gives slender, yellow needles of the *platinichloride*, $[\text{AuP}(\text{OMe})_3]_2\text{PtCl}_6$.

Aurotriethylphosphine chloride, $(\text{AuPEt}_3)\text{Cl}$, prepared by the action of triethylphosphine on auric chloride dissolved in alcohol, forms colourless needles, m. p. 80° , is stable in the air, and exhibits all the properties of a stable complex salt, since the gold is not precipitated by its ordinary reagents.

Aurotriphenylphosphine chloride, $(\text{AuPPh}_3)\text{Cl}$, prepared by the interaction of alcoholic solutions of triphenylphosphine and auric chloride, crystallises in colourless, truncated prisms, decomposes at $180-230^\circ$, and has the molecular weight 524—532 (calc. 494.6) in freezing benzene. It is stable in the air, and is not dissolved or decomposed by dilute nitric acid, concentrated hydrochloric acid, or potassium hydroxide solution. It forms the *platinichloride*, $(\text{AuPPh}_3)_2\text{PtCl}_6$, and the *sulphate*, $[\text{AuPPh}_3]_2\text{SO}_4$.

Methyl auroaminophosphite chloride, $[\text{AuP}(\text{OMe})_3(\text{NH}_3)_2]\text{Cl}$, forms microscopic, prismatic crystals, m. p. $75-76^\circ$.

Auroaminotriethylphosphine chloride, $[\text{AuPEt}_3(\text{NH}_3)_2]\text{Cl}$, forms microscopic, colourless prisms, decomposing at $90-150^\circ$.

Aurotriphenylphosphino chloride is quite insoluble in ammonia.

T. H. P.

Certain Homologues of Naphthalene. GUIDO BARGELLINI and G. MELACINI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 26—30).—The two *n*-propylnaphthalenes and the two *n*-butylnaphthalenes are obtained by treating a solution of naphthalene in carbon disulphide with *n*-propionyl chloride or *n*-butyryl chloride in presence of aluminium chloride, separating the isomeric α - and β -ketones thus obtained by means of picric acid, and reducing them with iodide, red phosphorus, and water (compare Claus, Abstr., 1892, 985; 1893, i, 162).

β -Naphthyl propyl ketone crystallises from alcohol in colourless, triclinic plates [A. ROSATI: $a:b:c = 0.6774:1:0.6029$; $\alpha = 94^\circ 31'$, $\beta = 140^\circ 3' 5'$, $\gamma = 90^\circ 27'$].

α -*n*-Propylnaphthalene, $\text{C}_{10}\text{H}_7\text{Pr}^a$, prepared by reducing α -naphthyl ethyl ketone, has b. p. $274-275^\circ$, and yields a *picrate*, m. p. $141-142^\circ$.

β -*n*-Propylnaphthalene, $\text{C}_{10}\text{H}_7\text{Pr}^a$, prepared by the reduction of β -naphthyl ethyl ketone, has b. p. $277-279^\circ$, and yields a *picrate*, m. p. $90-92^\circ$.

The β -propylnaphthalene prepared by Roux (Abstr., 1888, 1305) by the interaction of *n*-propyl bromide and a carbon disulphide solution of naphthalene in presence of aluminium chloride, is probably β -*iso*-propylnaphthalene, and results in consequence of isomeric change caused by the aluminium chloride.

α -*n*-Butylnaphthalene, $\text{C}_{10}\text{H}_7\cdot\text{CH}_2\text{Pr}^a$, obtained by reducing α -naphthyl propyl ketone, has b. p. $281-283^\circ$, and forms a *picrate*, m. p. $104-106^\circ$.

β -*n*-Butylnaphthalene, $\text{C}_{10}\text{H}_7\cdot\text{CH}_2\text{Pr}^a$, prepared by the reduction of

β -naphthyl propyl ketone, has b. p. 283—285°, and yields a *picrate*, m. p. 71—74°.

The β -butylnaphthalene, b. p. 280°, prepared by Wegscheider (Abstr., 1884, 1185) and by Baur-Thurgau (Abstr., 1894, i, 468) by the action of isobutyl chloride or bromide on naphthalene dissolved in carbon disulphide in presence of aluminium chloride, probably contains the tertiary butyl group; its *picrate* has m. p. 96°. T. H. P.

Equilibrium of Hydrogenation. MAURICE PADOA and UGO FARRIS (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 125—132. Compare this vol., i, 255).—The authors have made experiments to ascertain whether hydrogenated hydrocarbons, capable of giving up their hydrogen in several stages, can be made to do so by heating in presence of nickel at suitable temperatures.

When phenanthrene is hydrogenated in presence of nickel at 200°, dihydrophenanthrene and tetrahydrophenanthrene are obtained; at 175—200°, α -tetrahydrophenanthrene is formed; at 175°, dodecahydrophenanthrene is given, and at 150° a small quantity of a liquid which does not form a *picrate* and was not identified (compare Schmidt and Mezger, Abstr., 1907, i, 1022).

Dodecahydrophenanthrene only loses its hydrogen when heated with nickel at about 220°, at which temperature hexahydrophenanthrene also loses hydrogen, forming gaseous hydrocarbons and β -tetrahydrophenanthrene. At 280°, tetrahydrophenanthrene loses its hydrogen, yielding phenanthrene. In a closed tube at 250°, dodecahydrophenanthrene yields phenanthrene and gaseous hydrocarbons; at 330°, tetrahydrophenanthrene yields dihydrophenanthrene and gaseous hydrocarbons.

When heated in an open tube, decahydronaphthalene begins to lose hydrogen at 250°, naphthalene and gaseous hydrocarbons being formed. In a closed tube at 250°, decahydronaphthalene undergoes little change; at 300°, naphthalene is formed, together with gaseous hydrocarbons. When heated in a closed tube at 250° in presence of nickel, tetrahydronaphthalene is only partially dehydrogenated, gaseous hydrocarbons being formed, and probably also benzene or its homologues.

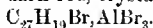
When decahydrofluorene is heated with nickel in an open tube at 250°, a slow evolution of gas is observed; at 300°, a more copious evolution of gas, mostly hydrogen, occurs. At 300° in a closed tube, hydrogen and gaseous hydrocarbons are evolved.

In an open tube at 250°, cyclohexene gives a large amount of gas, but in a closed tube at the same temperature, very little gas, mainly methane, is formed.

Thus, with hydrocarbons yielding several hydrogenated products, those most readily dehydrogenated by the action of nickel are those containing most hydrogen. Of the hydrocarbons examined, the only ones not attacked in this way are tetrahydronaphthalene at ordinary pressure and tetra- and dihydrophenanthrene under ordinary or increased pressure. The pressure has a marked influence on the dehydrogenating action of nickel, increased pressure generally causing increased action; with tetrahydronaphthalene, however, hydrogen is

eliminated at ordinary pressure, and gaseous hydrocarbons at about three atmospheres pressure. Gradual elimination of the hydrogen of a highly hydrogenated hydrocarbon cannot, as a rule, be effected by gradual rise of temperature; further, the elimination of hydrogen commences only at a temperature considerably higher than that at which the inverse change begins, and is complete, yielding the least highly hydrogenated compound. Hydrogenation and the inverse phenomenon are thus two distinct processes; in some cases, nickel can effect both these changes, but in others, it only acts as a catalyst for the reaction in one direction. With increase of pressure, however, the maximum temperature at which hydrogenation is possible, and the minimum temperature necessary for the inverse change, approach one another, so that hydrogenation becomes possible at temperatures at which it does not take place under ordinary pressure. Under increased pressure, then, the phenomenon becomes one of equilibrium, both hydrogenation and dehydrogenation taking place. Whether the nature of the catalyst influences this equilibrium is unknown. T. H. P.

Triphenylindene and Some of its Derivatives. ELMER P. KOHLER (*Amer. Chem. J.*, 1908, 40, 217—233).—In the preparation of diphenylbenzylidenacetophenone by boiling α -bromotriphenylpropionophenone with alcoholic potash (Abstr., 1907, i, 1054), a small amount of 1-ethoxy-1:2:3-triphenylindene is produced. This is formed by loss of water from the bromo-ketone and substitution of ethoxyl for bromine in the bromoindeno obtained, a process involving the shifting of the bromine atom from the α - to the β -position. 1-Bromo-1:2:3-triphenylindene, $C_6H_4 \begin{smallmatrix} \text{CBrPh} \\ \diagup \quad \diagdown \\ \text{CPh} \end{smallmatrix}$, is prepared by heating α -bromotriphenylpropionophenone (for which an improved method of preparation is given; compare Abstr., 1906, i, 754) to 150—160°. It separates from ether in large, transparent plates, m. p. 129°, and forms with aluminium bromide a dark red, crystalline compound,



1-Hydroxy-1:2:3-triphenylindene, prepared by adding water or sodium acetate to a hot solution of the bromo-derivative in acetic acid, forms lustrous prisms, m. p. 129°; the *methyl* ether crystallises in tablets, m. p. 153°, and the *ethyl* ether separates in large, lustrous prisms, m. p. 172°. On oxidation with a glacial acetic acid solution of chromic acid, the latter furnishes phthalophenone, colourless tablets, m. p. 148° (Zincke, Abstr., 1876, i, 703, gives yellow plates, m. p. 146°). 1:2:3-Triphenyl-1-ethylindene is obtained by the action of magnesium ethyl bromide on bromotriphenylindene; it crystallises in plates, m. p. 108°, and, on oxidation with cold chromic and acetic acids, yields *phenyl α -benzoylphenyl- α -phenyl-*n*-propyl ketone*, $C_6H_4Bz \cdot CEtPhBz$, crystallising in large, shining tablets, m. p. 180°, and giving phthalophenone and *o*-benzoylbenzoic acid when boiled with the oxidising agent. When a solution of bromotriphenylindene in benzene is shaken with zinc amalgam and the red solution allowed to evaporate in dry air, *triphenylindenyloxy peroxide*, $(C_{27}H_{19}O)_2$, is formed. It crystallises in small, shining prisms, decomposing at about 155°. From its sulphuric acid solution, water precipitates some hydroxytriphenylindene and

alcohol, ethoxytriphenylindene. 1:2:3-Triphenylindene is prepared by treating an ethereal solution of the bromo-derivative with magnesium and a trace of iodine in an atmosphere of hydrogen and dissolving the excess of magnesium with hydrochloric acid. It crystallises from ether or acetone in large, colourless prisms, m. p. 135°. When treated with bromine vapour at 150—160°, the bromo-derivative is regenerated. On oxidation with chromic and acetic acids, at the ordinary temperature the chief product is the hydroxy-derivative, but when the mixture is boiled, phthalophenone is exclusively formed. 1:1:3-Triphenylindene is the hydrocarbon obtained by Vorländer and Siebert (Abstr., 1906, i, 346) from tetraphenylallene, and the constitution suggested by these authors is now shown to be correct. The oxidation product obtained by them is phthalophenone; when, however, the oxidation with chromic and acetic acids is carried out in the cold, *o*-benzoyltriphenylacetic acid, $C_6H_5Bz \cdot CPh_2 \cdot CO_2H$, is formed. This crystallises in small prisms, m. p. 230° (decomp.); the sodium salt crystallises in small, colourless prisms, m. p. 130° (decomp.).

J. C. C.

Studies in Nitration. III. Nitration of Aniline and of Certain of its *N*-Alkyl, *N*-Aryl, and *N*-Acyl Derivatives. J. BISHOP TINGLE and F. C. BLANCH (J. Amer. Chem. Soc., 1908, 30, 1395—1412. Compare Abstr., 1907, i, 120; this vol., i, 408).—The authors have extended their work on nitration with 80% nitric acid (D 1.46) in presence of acetic, oxalic, trichloroacetic, or 92% sulphuric acid (D 1.83). Except when sulphuric acid is used, methyl- or ethylaniline yields tars, and the formation of tar was the general result of the nitration of dimethyl- or diethyl-aniline under similar conditions. Dimethylaniiline, when nitrated in presence of a mixture of oxalic and acetic acid, gives *p*-nitrodimethylaniline. Formanilide yields *p*-nitroformanilide when nitrated in the presence of sulphuric acid, and, under the same conditions, acetanilide gives *m*-nitroacetanilide, but in the presence of oxalic or trichloroacetic acid, *p*-nitroacetanilide is formed. On nitrating benzanilide in the presence of sulphuric acid or a mixture of oxalic and acetic acids, the para-derivative is obtained, but in the presence of acetic acid the meta-derivative results. The products of nitration of a number of other anilides have not yet been identified.

J. C. C.

Iodination of *m*-Nitroaniline by means of Iodine and Potassium Iodate. WILHELM KÖRNER and BELASIO (Atti R. Accad. Lincei, 1908, [v], 17, ii, 679—690).—*m*-Nitroaniline is readily iodinated by adding iodine dissolved in 25% aqueous potassium hydroxide to a solution of the base in hydrochloric acid containing potassium iodate; using 1 mol. of iodine per mol. of base, a mixed product is obtained containing 8% of 4-iodo-3-nitroaniline, 36% 6-iodo-3-nitroaniline, 17% 4:6-di-iodo-3-nitroaniline, and 39% of 2:4-di-iodo-3-nitroaniline. The structure of these substances follows from the facts given below.

4-Iodo-3-nitroaniline crystallises from alcohol in orange needles, m. p. 142°, and gives an acetyl derivative, m. p. 136.5°; the two substances are isomorphous with 4-bromo-3-nitroaniline and its acetyl

derivative respectively. On replacing the amino-group by hydrogen, *o*-iodonitrobenzene is obtained; on replacing the same group by iodine, 1:4-di-iodo-2-nitrobenzene (Brenans, Abstr., 1902, i, 673) is formed.

6-Iodo-3-nitroaniline crystallises from alcohol in orange-yellow needles, m. p. 160.4°, and is convertible into *p*-iodonitroaniline by the diazo reaction. 6-Iodo-3-nitroacetanilide crystallises from alcohol in slender, white needles, m. p. 199°.

2:4-Di-iodo-3-nitroaniline (Brenans, Abstr., 1904, i, 661), m. p. 125°, gives an *acetyl* derivative crystallising in white, nacreous prisms, m. p. 168°.

4:6-Di-iodo-3-nitroaniline forms stellate aggregates of slender, pale yellow needles, m. p. 149°, and gives 1:3-di-iodo-4-nitrobenzene on eliminating the amino-group; replacing the same group by iodine, 1:2:4-tri-iodo-5-nitrobenzene, m. p. 178°, is obtained. This crystallises from carbon disulphide in yellow needles, and, on reduction with ferrous sulphate and ammonia, gives 2:4:5-tri-iodoaniline, which crystallises from a mixture of alcohol and ether in long, white, silky needles, m. p. 117.8°, gives an *acetyl* derivative, m. p. 241.5°, and, on eliminating the amino-group, is converted into the 1:2:4-tri-iodobenzene, m. p. 91.4°; the latter substance is also obtained from 1:4-di-iodo-2-nitrobenzene by reduction and the diazo-reaction, thus confirming its structure. The same 1:2:4-tri-iodobenzene can also be obtained from 2:4-di-iodo-3-nitroaniline (*supra*) by replacing the amino-group by iodine, reducing the nitro-group, and then replacing the amino-radicle by hydrogen.

When 4-iodo-3-nitroaniline is iodinated by means of iodine and potassium iodate, 65% of the product consists of 2:4-di-iodo-3-nitroaniline and 35% of 4:6-di-iodo-3-nitroaniline.

1:2:3-Tri-iodobenzene is obtained by converting 2:4-di-iodo-3-nitroaniline into 1:3-di-iodo-2-nitrobenzene (Brenans, *loc. cit.*) by the diazo-reaction, reducing the product to 2:6-di-iodoaniline, m. p. 122°, and decomposing the diazo-sulphate derived from the latter by potassium iodide; 1:2:3-tri-iodobenzene crystallises in small, white prisms, m. p. 116°.

1:2:4:5-Tetraiodobenzene, obtained by replacing the amino-group of 2:4:5-tri-iodoaniline by iodine, crystallises from acetic acid or benzene in white needles, m. p. 254°.

1:3:4-Tri-iodo-2-nitrobenzene, prepared from 2:4-di-iodo-3-nitroaniline by the diazo-reaction, crystallises from carbon disulphide in long, white prisms, m. p. 137°, and, on reduction with ferrous sulphate and ammonia, gives 2:3:6-tri-iodoaniline, crystallising in stellate aggregates of needles and melting at 116.8°. 1:2:3:4-Tetra-iodobenzene, obtained from this by the diazo-reaction, crystallises from carbon disulphide and melts at 136°.

W. A. D.

[Preparation of 3-Chloro-4-aminodimethylaniline.] FARBEN-FABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 197035).—3-Chloro-4-aminodimethylaniline, white crystals, m. p. 42°, b. p. 158°/15 mm., is prepared by reducing the nitroso-derivative of 3-chlorodimethylaniline; its diazo-salt complexes with 1:8-dihydroxynaphthalene-3:6-

disulphonic acid, giving rise to a blue colouring matter. 3 *Chloro-4-aminodimethylaminis*, colourless liquid, b. p. 285°/760 mm., forms a similar blue azo-dye.

G. T. M.

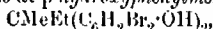
Characteristic Colour Reactions Produced by Sodium Hypobromite. WILLIAM M. DEHN and SILAS F. SCOTT (*J. Amer. Chem. Soc.*, 1908, 30, 1418—1423. Compare this vol., ii, 907).—Sodium hypobromite solution, either alone or preceded by ammonia, gives characteristic colorations with phenols and aromatic amines. The reactions of a large number of phenols, aromatic amines, and alkaloids are described. Isomeric compounds may readily be distinguished by this means.

J. C. C.

Action of Bromine and Chlorine on Phenols. Substitution Products, ψ -Bromides, and ψ -Chlorides. XXIII. Action of Bromine on Di-*p*-hydroxyphenylmethylethylmethane; ψ -Bromides and Quinones of *p*-sec.-Butylphenol. THEODOR ZINCKE and J. GOLDEMANN (*Annalen*, 1908, 362, 201—220. Compare Zincke and von Hohorst, *Abstr.*, 1907, i, 614).—The interesting results obtained during the investigation on the behaviour of di-*p*-hydroxyphenyl-dimethylmethane towards bromine (compare Zincke and Grüters, *Abstr.*, 1906, i, 172) have led to a similar investigation on di-*p*-hydroxyphenylmethylethylmethane. The two compounds behave in the same manner; the heptabromide obtained from the higher homologue is, however, far more stable than the corresponding compound derived from the lower homologue.

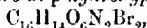
Di-*p*-hydroxyphenylmethylethylmethane, $\text{CMeEt}(\text{C}_6\text{H}_4\cdot\text{OH})_2$, is prepared by the action of hydrogen chloride on a mixture of methyl ethyl ketone (1 part) and phenol (3 parts); it crystallises in colourless needles or prisms, m. p. 124—125°; the *dibenzoate*, $\text{C}_{20}\text{H}_{20}\text{O}_4$, crystallises in white needles, m. p. 140—141°; the *diacetate* could not be obtained in a solid state.

3:5:3':5'-Tetrabromo-di-*p*-hydroxyphenylmethylethylmethane,



prepared by the action of bromine in glacial acetic acid on the parent phenol, crystallises in thick, white needles, m. p. 155°; the *diacetate*, $\text{C}_{20}\text{H}_{18}\text{O}_4\text{Br}_4$, crystallises in white needles, m. p. 174°. The tetrabromide is converted by nitric acid (D 1.4—1.5) in acetic acid into 2:6-dibromo-4-nitrophenol, $\text{C}_6\text{H}_3\text{O}_3\text{NBr}_2$, m. p. 139—140°, and 2-bromo-4:6-dinitrophenol, pale yellow needles, m. p. 118—119°. Boiling nitric acid converts the tetrabromide into picric acid.

3:3'-Dibromo-5:5'-dinitro-di-*p*-hydroxyphenylmethylethylmethane,



is formed by adding solid sodium nitrite to a solution of the tetrabromide in glacial acetic acid; it forms small, compact, yellow crystals, m. p. 146—147°, and yields soluble, yellowish-red alkali and ammonium salts and insoluble, intensely red barium and calcium salts; the *diacetate*, $\text{C}_{20}\text{H}_{12}\text{O}_8\text{N}_2\text{Br}_2$, crystallises in yellowish-white needles, m. p. 144—145°.

ψ -*p*-Tribromo-sec.-butyltribromophenol (ψ -hexabromo-*p*-sec.-butyl-

phenol), $\text{CO} \begin{smallmatrix} \text{CBr}:\text{CBr} \\ \text{CBr}=\text{CH} \end{smallmatrix} \text{CH} \cdot \text{CBrEt} \cdot \text{CHBr}_2$, is formed together with tribromophenol when the tetrabromide described above is treated with bromine at the ordinary temperature; it crystallises in small, colourless, glistening prisms, m. p. 154—155°. *Acetylhexabromo-p-sec.-butylphenol*, $\text{C}_{18}\text{H}_{10}\text{O}_2\text{Br}_6$, crystallises in colourless prisms, m. p. 142°.

p-Dibromo-sec.-butylidenetribromoquinone (*pentabromo-sec.-butylidenequinone*), $\text{CO} \begin{smallmatrix} \text{CBr}:\text{CBr} \\ \text{CBr}=\text{CH} \end{smallmatrix} \text{C}:\text{CEt} \cdot \text{CHBr}_2$, prepared by shaking an ethereal solution of the hexabromide just described with a 10% aqueous solution of sodium acetate, crystallises in yellow prisms, m. p. 182—183°. It is converted by acetic anhydride and strong sulphuric acid at the ordinary temperature into *p-α-dibromo-β-acetoxy-sec.-butyltribromophenyl acetate*, $\text{OAc} \cdot \text{C}_6\text{H}_3\text{Br}_3 \cdot \text{CEt}(\text{OAc}) \cdot \text{CHBr}_2$, which crystallises in colourless, glistening prisms or plates, m. p. 164—165°.

ψ-p-Tribromo-sec.-butyltetrabromophenol (*ψ-heptabromo-p-sec.-butylphenol*), $\text{CO} \begin{smallmatrix} \text{CBr}:\text{CBr} \\ \text{CBr}:\text{CBr} \end{smallmatrix} \text{CH} \cdot \text{CBrEt} \cdot \text{CHBr}_2$, is formed together with tribromophenol by the action of bromine on the tetrabromide described above at 100°; it crystallises in brilliant, colourless needles, m. p. 190—191° (decomp.); the *acetate*, $\text{C}_{12}\text{H}_9\text{O}_2\text{Br}_7$, crystallises in colourless, glistening prisms, m. p. 130—131°.

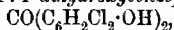
p-Dibromo-sec.-butylidenetetrabromoquinone (*hexabromo-sec.-butylidenequinone*), $\text{CO} \begin{smallmatrix} \text{CBr}:\text{CBr} \\ \text{CBr}:\text{CBr} \end{smallmatrix} \text{C}:\text{CEt} \cdot \text{CHBr}_2$, may be prepared by shaking an ethereal solution of the heptabromide with an aqueous solution of sodium carbonate, but not sodium acetate; it is obtained in a purer state by boiling a solution of the heptabromide in benzene with anhydrous sodium carbonate; it crystallises in small, yellow prisms, m. p. 174—175°. Acetic anhydride and concentrated sulphuric acid convert it into *α-dibromo-β-acetoxy-p-sec.-butyltetrabromophenyl acetate*, $\text{OAc} \cdot \text{C}_6\text{Br}_4 \cdot \text{CEt}(\text{OAc}) \cdot \text{CHBr}_2$; it forms small, granular crystals, which soften at 70°, m. p. 90°. W. H. G.

Action of Bromine and Chlorine on Phenols; Substitution Products, ψ-Bromides, and ψ-Chlorides. XXIV. Tetrachloro- and Tetrabromo-dihydroxybenzhydrol and their Transformation Products. THEODOR ZINCKE and E. BIRSCHER (*Annalen*, 1908, 362, 221—241. Compare preceding abstract).—It has been shown by Zincke and Krügener (*Abstr.*, 1904, i, 401) that a hexabromohydroxybenzylidenequinone can be prepared from 2:3:5:2':3':5'-hexabromo-4:4'-dihydroxybenzhydrol. Attempts were therefore made to prepare, by similar means, a hydroxybenzylidenequinone, but without success, since 4:4'-dihydroxybenzhydrol could not be prepared (compare von Baeyer and Burkhardt, *Abstr.*, 1882, 637). 3:5:3':5'-Tetrabromo-4:4'-dihydroxybenzhydrol and the corresponding tetrachloro-compound were, however, prepared, and were found to behave like the hexabromo-derivative.

3:5:3':5'-Tetrabromo-4:4'-dihydroxybenzopbenone has m. p. 225—226°; von Baeyer and Burkhardt give m. p. 213—214° (*loc. cit.*)

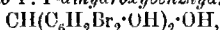
It is converted by bromine at 150—160° into pentabromophenol, and by nitric acid in acetic acid into 2-bromo-4:6-dinitrophenol. 3:3'-*Dibromo-5:5'-dinitro-4:4'-dihydroxybenzophenone*, $C_{13}H_6O_7N_2Br_2$, is prepared by adding solid sodium nitrite to a solution of the tetrabromide in glacial acetic acid; it crystallises in yellow needles, m. p. 246°, and forms orange alkali salts; the *diacetate*, $C_{17}H_{10}O_9N_2Br_2$, forms small, compact, pale yellow crystals, m. p. 165°.

3:5:3':5'-*Tetrachloro-4:4'-dihydroxybenzophenone*,



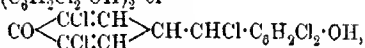
obtained by passing chlorine into a solution of 4:4'-dihydroxybenzophenone in acetic acid, crystallises in colourless leaflets or needles, m. p. 231—232°; the *diacetate*, $C_{17}H_{10}O_5Cl_4$, forms slender needles, m. p. 196—197°.

3:5:3':5'-*Tetrabromo-4:4'-dihydroxybenzhydrol*,



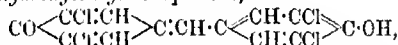
is obtained by reducing the tetrabromodihydroxybenzophenone with zinc dust and acetic acid; it crystallises in colourless needles, m. p. 173—174° (decomp.), and is oxidised by bromine or calcium hypobromite to the parent substance.

3:5:3':5'-*Tetrachloro-4:4'-dihydroxybenzhydrol*, $C_{18}H_8O_3Cl_4$, crystallises in small, compact needles, m. p. 179° (decomp.); the *triacetate*, $C_{18}H_4O_6Cl_4$, crystallises in small, glistening plates, m. p. 123—124°. Tetrachlorodihydroxybenzhydrol is converted by a solution of hydrogen chloride in glacial acetic acid into ψ -pentachloro-p-dihydroxydiphenylmethane, $CHCl(C_6H_2Cl_2\cdot OH)_2$ or



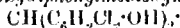
crystallising in colourless needles, m. p. 134—135°. It is reduced by zinc and hydrogen chloride in ethereal acetic acid to tetrachloro-p-dihydroxydiphenylmethane. The *diacetate*, $CHCl(C_6H_2Cl_2\cdot OAc)_2$, prepared by the action of acetyl chloride on the ψ -pentachloride, crystallises in small, thick, colourless needles, m. p. 93°.

Tetrachlorohydroxybenzylidenequinone,

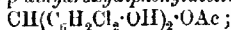


prepared by shaking with warm water a solution of the ψ -pentachloride in a mixture of benzene and light petroleum, is obtained as a red powder, which sinters at 200°, m. p. about 220°. The product so obtained is not quite pure, and apparently contains H_2O , which is slowly liberated in a vacuum at 80—90°; it quickly becomes yellowish-white under the action of light, due to the absorption of water. The sodium salt is deep violet.

Tetrachloro-p-dihydroxydiphenylmethoxymethane,



is formed by dissolving the ψ -pentachloride described above in methyl alcohol; it crystallises in thick, colourless needles, m. p. 142°; the *diacetate*, $C_{18}H_{11}O_5Cl_4$, forms small prisms or plates, m. p. 155°. The ψ -pentachloride is converted by boiling acetic acid and sodium acetate into *tetrachloro-p-dihydroxydiphenylacetoxymethane*,



t forms compact, colourless crystals, m. p. 171° (decomp.); the sodium salt is brownish-red with a green reflex.

ψ -Pentabromo-p-dihydroxydiphenylmethane, $\text{CHBr}(\text{C}_6\text{H}_2\text{Br}_2\text{-OH})_2$, obtained by the addition of hydrogen bromide to the tetrabromodihydroxybenzhydrol described above, crystallises in small, colourless plates, m. p. 164—165°. It is not converted by acetic anhydride into the normal acetyl derivative, but into tetrabromo-p-dihydroxybenzhydrol triacetate; this substance could not be obtained pure.

Tetrabromohydroxybenzylidenequinone, $\text{O}:\text{C}_6\text{H}_2\text{Br}_2:\text{CH}\cdot\text{C}_6\text{H}_2\text{Br}_2\text{-OH}$, prepared by adding water to a solution of the ψ -pentabromide in acetone, is a red powder, m. p. 205°; the sodium salt is deep violet. The tetrabromoquinone, when warmed with aqueous acetone, readily combines with water, forming the corresponding tetrabromodihydroxybenzhydrol. It is also converted by methyl alcohol into tetrabromodihydroxydiphenylmethoxymethane, $\text{CH}(\text{C}_6\text{H}_2\text{Br}_2\text{-OH})_2\cdot\text{OMe}$, colourless crystals, m. p. 143—144°.

W. H. G.

Oxidation of isoeugenol. Dehydrodiisoeugenol. HENRI COUSIN and HENRI HÉRISSEY (*Compt. rend.*, 1908, 147, 247—249; *J. Pharm. Chim.*, 1908, [vi], 28, 193—199. Compare *ibid.*, 146, 1413).—When isoeugenol (20 c.c.), dissolved in 95% alcohol (180 c.c.), is treated with 40 c.c. ferric chloride solution (D 1.26) and with 120 c.c. of water, the greenish-blue mixture gradually becomes lighter in colour, and deposits light rose-coloured needles, which become colourless when washed with alcohol. The substance crystallises in long, colourless needles or rosettes of flat plates, m. p. 133°, which dissolve in alkali hydroxide solutions. The alcoholic solution gives a greenish-blue coloration with ferric chloride. Results of analysis and a cryoscopic determination of the molecular weight indicate that the substance is dehydrodiisoeugenol, $\text{C}_{20}\text{H}_{22}\text{O}_4$. The oxidation can be effected with ferric chloride in aqueous solution, but with less satisfactory results, and by the action of a current of air on an aqueous solution of the phenol containing a small proportion of a maceration of *Russula delica* in glycerol.

Dimethyldehydrodiisoeugenol, obtained by the action of methyl sulphate on the phenol in the presence of potassium hydroxide, crystallises in thin, nacreous, colourless lamellae, m. p. 126° (corr.).

Diacetyldehydrodiisoeugenol, prepared by heating dehydrodiisoeugenol with acetic anhydride and fused sodium acetate, forms dense, massive, white crystals, m. p. 114° (corr.).

Dibenzoyldehydrodiisoeugenol, obtained by treating the phenol with benzoyl chloride in the presence of potassium hydroxide, crystallises in spheres of colourless, radiate needles, m. p. 119—120° (corr.).

The three ethers are insoluble in water and alkalis, do not give any coloration with ferric chloride, but reduce an aqueous solution of potassium permanganate.

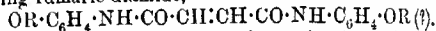
E. H.

Maleic and Fumaric Derivatives of p-Aminophenols. ARNALDO PRATTI (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 635—641).—In benzene solution, maleic anhydride, like other anhydrides of dibasic

acids, reacts with *p*-aminophenols, forming additive compounds, substituted amic acids, which, unlike the corresponding compounds formed with saturated aliphatic and aromatic anhydrides, are yellow and give a violet coloration with ferric chloride in aqueous-alcoholic solution when the hydrogen of the phenolic hydroxyl is replaced by an alkyl radicle. It is hence probable that these amic acids have the enolic constitution $\text{OR} \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{C}(\text{OH}) \cdot \text{CH} : \text{CH} \cdot \text{CO}_2\text{H}$. They do not, however, yield substituted carbamates when treated with phenyl-carbimide in presence of toluene in the cold, whilst, when heated, decomposition occurs with formation of maleic anhydride and a mono-substituted diphenylcarbamide: $\text{OR} \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{C}(\text{OH}) \cdot \text{CH} : \text{CH} \cdot \text{CO}_2\text{H} + \text{NPh} : \text{CO} = \frac{\text{CH} \cdot \text{CO}}{\text{CH} \cdot \text{CO}} \text{O} + \text{NHPh} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{OR}$. This reaction does

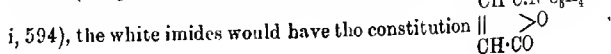
not exclude the possibility of the presence of a hydroxyl group, since hydroxylic compounds are known which do not react with phenyl-carbimide, and it is also possible that the above reaction represents the decomposition of the carbamate at the high temperature used.

When maleic anhydride or acid is fused with a *p*-aminophenol at 125—130°, a small quantity of the maleinamate or fumaramate of the aminophenol is formed, together with a large proportion of the corresponding fumaric diamide,



These compounds may undergo transformation into the enolic form, $\text{OR} \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{C}(\text{OH}) \cdot \text{CH} : \text{CH} \cdot \text{C}(\text{OH}) : \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{OR}$, and they can, indeed be obtained in two modifications, one white and the other yellow. But these two forms can be readily converted into one another, the white into the yellow by trituration in a mortar, and the yellow into the white by the addition of water to its sulphuric acid solution, so that they are best regarded as physical or enantiotropic isomerides. That these compounds are fumaric derivatives is shown by the fact that they are also obtained by heating the acid or normal fumarates of the amino-phenols.

When heated, the amic acids obtained from maleic anhydride and *p*-aminophenols yield, not the corresponding imides, but fumaric diamides. The imides of these amic acids, which can be obtained in presence of dehydrating agents, cannot be converted into their enantiotropic forms either mechanically or by crystallisation, and, even at 360°, are not appreciably decomposed or converted into the isomeric compounds. But when the white imides are kept fused at 130—140° in a current of dry carbon dioxide, they are partly transformed into yellow isomeric imides, which have higher melting points than the white modifications, and can be readily obtained by heating the corresponding maleinamino-acids at 170—180° in a stream of dry carbon dioxide. Since mixtures of these imides melt at a lower temperature than either separately, they are not enantiotropic forms, but chemical isomerides. Assuming that the action of acetylchloride or phosphoryl chloride on amic acids yields asymmetric imides or isomerides (compare Hooogewerff and van Dorp, Abstr., 1893, i, 599; 1894, i, 594), the white imides would have the constitution



and the yellow ones, $\begin{smallmatrix} \text{CH}\cdot\text{CO} \\ | \\ \text{CH}\cdot\text{CO} \end{smallmatrix} > \text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OR}$. The yellow imides dissolve in alkali alkoxide solutions, giving a faint yellow coloration, whilst the white isomerides yield an intense violet coloration, due to the formation of additive products containing 1 mol. of imide to 1 mol. of alkoxide.

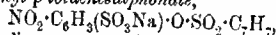
Acetic anhydride decomposes the maleinamic acids into maleic anhydride and acetyl derivatives of the aminophenols. The phenacetin obtained in this way from *p*-ethoxyphenylmaleinamic acid always contains an orange-yellow compound, m. p. 155—157°, with which it forms a solid solution.

T. H. P.

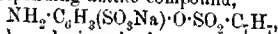
Preparation of 2-Aminophenol-5-sulphonic Acid. LEOPOLD CASSELLA & Co. (D.R.-P. 197496).—The sulphonation of *o*-aminophenol with fuming sulphuric acid yields exclusively 2-aminophenol-4-sulphonic acid. An isomeric 2-aminophenol-5-sulphonic acid, white needles, is obtained by sulphonating carboxy-*o*-aminophenol and hydrolysing the product with aqueous sodium hydroxide. The diazo-derivative, yellow needles, is only moderately soluble in water, and, on boiling with alcohol, yields phenol-3-sulphonic acid.

G. T. M.

Preparation of Arylsulphonates of 2-Aminophenol-4-sulphonic Acid. LEOPOLD CASSELLA & Co. (D.R.-P. 195226).—Sodium *p*-sulpho-2-nitrophenyl-*p*-toluenesulphonate,



prepared from sodium *o*-nitrophenol-4-sulphonate and *p*-toluenesulphonyl chloride in aqueous sodium hydroxide, crystallises in yellow leaflets. The corresponding amino-compound,



leaflets, is obtained by reducing the foregoing compound with iron and dilute acetic acid, and treating the products with sodium carbonate; it forms a very reactive, insoluble diazo-derivative.

G. T. M.

Preparation of 3-Nitro 6-aminophenol-4-sulphonic Acids. FARDWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 197807).—4-Chloro-2-aminophenol-4-sulphonic, 2-amino-*o*-cresol-4-sulphonic, and 2-amino-*p*-cresol-2-sulphonic acids readily yield carbonyl derivatives on treatment with carbonyl chloride in alkaline solutions. The sodium salts of these carbonyl compounds are colourless, soluble, crystalline substances, which, on nitration, furnish nitro-derivatives containing the nitro-group in the para-position to the amino-group. These products, on hydrolysis with aqueous calcium hydroxide, give rise to 2-chloro-3-nitro-6-aminophenol-4-sulphonic, 6-nitro-3-amino-*o*-cresol-5-sulphonic, and 2-nitro-6-amino-*p*-cresol-3-sulphonic acids, which form yellow, soluble alkali salts and diazo-derivatives.

G. T. M.

Preparation of the Leuco-derivative of Colouring Matter obtained by Oxidation from 3-Hydroxy-(1)-thionaphthens. KALLE & Co. (D.R.-P. 196501).—When reduced with alkali hyposulphite or dextrin, the colouring matter derived from 3-hydroxy-(1)-thionaphthen furnishes a leuco-derivative, soluble in alkalis, but

precipitated by acids. The leuco-compound is sparingly soluble in water, and oxidises only slowly to the colouring matter on exposure to the atmosphere; it forms a soluble sodium salt, crystallising in lustrous, colourless leaflets.

G. T. M.

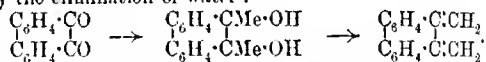
Leucoalizarin (1:2-Dihydroxyanthranol). EUGÈNE GRAND-
MOUGIN (*Chem. Zentr.*, 1908, i, 2179; from *Rev. Gén. Mat. color.*, 1908,
12, 44).—This substance, $C_6H_4 \begin{smallmatrix} C(OH) \\ | \\ C(OH) \end{smallmatrix} C_6H_2(OH)_2$, is prepared by
reducing alizarin in very dilute sodium hydroxide solution by means
of sodium hydrogen sulphite; it crystallises in small, brown plates,
m. p. 150°.

J. V. E.

Preparation of o-Nitrosobenzyl Alcohol and Anthranil. KALLE & Co. (D.R.-P. 194811).—o-Nitrotoluene when heated with aqueous sodium hydroxide at 170°, and subsequently distilled, furnishes an oil which, on treatment with alcoholic mercuric chloride, gives rise to a white, flocculent precipitate, which probably consists of the mercurichloride of o-nitrosobenzyl alcohol, from which the latter substance can be liberated by the successive action of concentrated hydrochloric acid and water. The filtrate from the foregoing precipitate contains anthranil, which is set free by strong hydrochloric acid from the concentrated solution.

G. T. M.

Ditertiary Alcohols from Phenanthraquinone. THEODOR ZINCKE and W. TROPP (*Annalen*, 1908, 362, 242—259).—From the investigations of Zincke and Buff (*Abstr.*, 1905, i, 880), it seemed probable that quinonoid hydrocarbons might be obtained from the ditertiary alcohols derived from phenanthraquinone (dihydroxydialkyl-dihydrophenanthrenes; compare Werner and Grob, *Abstr.*, 1904, i, 864) by the elimination of water:

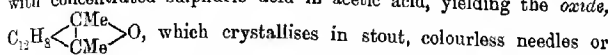


The hydroxy-derivatives do not, however, lose 2H₂O, but pass into oxides with the elimination of 1H₂O. That the compounds so formed

have the formula $\begin{smallmatrix} C_6H_4 \cdot CR \\ | \\ C_6H_4 \cdot CR \end{smallmatrix} > O$ is supported by the fact that they do not yield hydrazones or oximes, and are converted on reduction into 9:10-dialkylphenanthrenes. The latter are oxidised by chromic acid to diketones, R·CO·C₆H₄·C₆H₄·CO·R; the same diketones are formed by oxidising the parent dihydroxy compounds. Dihydroxydimethyldihydrophenanthrene is converted by phosphorus pentachloride into the corresponding oxide and a chloride which probably has the formula $\begin{smallmatrix} C_6H_4 \cdot CMeCl \\ | \\ C_6H_4 \cdot C \cdot CH_2 \end{smallmatrix}$. The analogous ethyl, propyl, and benzyl compounds, when similarly treated, yield only oxides.

9:10-Dihydroxydimethyldihydrophenanthrene, $C_{12}H_8 \begin{smallmatrix} CMe \cdot OH \\ | \\ CMe \cdot OH \end{smallmatrix}$, prepared by adding an ethereal solution of phenanthraquinone to an

etheral solution of magnesium methyl iodide and treating the additive product so formed with dilute sulphuric acid, crystallises in large, colourless, pointed prisms, m. p. 164°; neither an acetyl nor a benzoyl derivative could be prepared. It loses $1\text{H}_2\text{O}$ when treated with concentrated sulphuric acid in acetic acid, yielding the oxide,



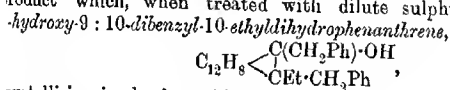
prisms, m. p. 75°. The oxide is reduced by red phosphorus and hydriodic acid to 9:10-dimethylphenanthrene, $\text{C}_{16}\text{H}_{14}$, crystallising in colourless, pointed prisms, m. p. 139°. 9:10-Dihydroxydimethylidihydrophenanthrene is converted by phosphorus pentachloride into the oxide just described and a chloride, $\text{C}_{16}\text{H}_{13}\text{Cl}$, obtained as colourless, spear-shaped crystals, m. p. 155°. It loses hydrogen chloride when heated with an alcoholic solution of potassium hydroxide, yielding a substance which crystallises in white needles, m. p. 94–95°.

The following compounds are obtained by the same methods as the corresponding methyl derivatives.

9:10-Dihydroxydiethylidihydrophenanthrene, $\text{C}_{18}\text{H}_{20}\text{O}_2$, crystallises in microscopic, delicate needles, m. p. 120–122°. The corresponding oxide, $\text{C}_{18}\text{H}_{18}\text{O}$, crystallises in large plates or long, thin prisms, m. p. 65°; it yields, on reduction, 9:10-diethylphenanthrene (4), crystallising in silvery leaflets, m. p. 105–106°.

9:10-Dihydroxydipropylidihydrophenanthrene, $\text{C}_{20}\text{H}_{24}\text{O}_2$, forms large, hard prisms, m. p. 155–156°. The oxide, $\text{C}_{20}\text{H}_{22}\text{O}$, crystallises in prisms, m. p. 83°; it is not reduced by hydriodic acid and red phosphorus.

9:10-Dihydroxydibenzylidihydrophenanthrene, $\text{C}_{28}\text{H}_{24}\text{O}_2$, crystallises in asymmetric prisms, m. p. 175°. The oxide, $\text{C}_{28}\text{H}_{22}\text{O}$, forms compact needles and pointed prisms, m. p. 143°; it is not attacked by phosphorus pentachloride under pressure at 150°, but is reduced by hydriodic acid and red phosphorus at 160° to phenanthrene. The oxide reacts with magnesium ethyl bromide, forming an additive product which, when treated with dilute sulphuric acid, yields



crystallising in slender, white needles, m. p. 186–187°. W. H. G.

Comparative Experiments on the Basicity and Strength of Acids and Phenols. ALFRED THIEL and HERMANN RÖMER (*Zeitsch. physikal. Chem.*, 1908, 63, 711–761. Compare Thiel, Schumacher, and Römer, *Abstr.*, 1906, i, 22).—The method used by the authors consists in studying the changes in conductivity which result from the gradual addition of sodium hydroxide to a standard quantity (generally 1 millimole) of an acid in dilute solution (compare Miotati, *Abstr.*, 1900, ii, 214; Küster and Grütters, *Abstr.*, 1903, ii, 611; Küster, Grütters, and Geibel, *Abstr.*, 1905, ii, 55). If the value of the conductivity is plotted against the number of c.c. of sodium hydroxide added, the curve obtained in the case of a strong monobasic acid falls rapidly to a minimum, which coincides with the neutralisation point,

If the monobasic acid is of medium strength, the curve falls a little to a rounded minimum and then rises to the neutralisation point, which is marked by a break in the curve; if the monobasic acid is very weak, no minimum at all is observed, the curve rising from the beginning, and the neutralisation point being marked by a break. It is pointed out that in the case of monobasic acids of medium strength, the weaker the acid the nearer must the minimum lie to the beginning of the curve. Each such acid must at the minimum point be dissociated to the extent of about 15%; the more dilute the solution in which any one such acid is examined the less is the distance between the point of minimum conductivity and the neutralisation point.

The authors discuss also the form of curve which is to be expected when a mixture of two monobasic acids of different strengths or a dibasic acid is gradually neutralised by sodium hydroxide. In the latter case, it is sometimes advantageous to titrate back with a strong acid, as the neutralisation point is then less liable to be obscured by hydrolysis. These more complicated types of curve are illustrated by the authors' experiments with hydrochloric acid + acetic acid, monochloroacetic acid + acetic acid, oxalic, fumaric, maleic, succinic, and phosphoric acids. It is noteworthy that phosphoric acid is found to behave as a dibasic acid (contrast Küster, Grütters, and Geibel, *loc. cit.*).

The authors have made an exhaustive study of the behaviour of aromatic hydroxylic compounds on the lines just indicated, and they draw conclusions as to the way in which the acidic character of the -OH group is modified by the introduction of other substituent groups into the molecule. The following are some of the main conclusions reached.

A compound containing two -OH groups in the *o*-position is monobasic, and the strength is only very slightly greater than that of the corresponding compound with one such group. When the second -OH group is in the meta- or para-position, the substance is dibasic, but the acidic character of the second group is exceedingly feeble. The introduction of nitro-groups markedly increases the acidic power of the -OH group, and the curves obtained by the gradual neutralisation of *o*-nitrophenol, 2:4-dinitrophenol, and picric acid may be taken as examples of the three types mentioned in the beginning of this abstract.

The introduction of a sulphonic group (as in sodium phenol-sulphonate) in the ortho- or para-position immensely strengthens the acidic character of the -OH group. In nitro-derivatives of the phenol-sulphonic acids, the acidic character of the -OH group is notably greater than in the corresponding nitrophenols. The -CHO group, as shown for example by the behaviour of salicylaldehyde, makes a phenol more distinctly acid. An -OH group in the ortho-position to a carboxyl group is indifferent; in the meta- and para-positions it has an appreciably acid character. For further information as to the influence of these substituents on the acidic character of one or more -OH groups, the original must be consulted.

In one or two favourable cases where the phenolic substance is an acid of medium strength, it is possible to calculate its dissociation constant from the position of the point of minimum conductivity. J. C. P.

Influence of Catalytic Agents in Ester Formation. Hydrogen Bromide and Zinc Bromide in the Formation of Ethyl Benzoate. ISAAC K. PHELPS, M. A. PHELPS, and E. A. EDDY (*Amer. J. Sci.*, 1908, [iv], 26, 281—289).—The rate of esterification of benzoic acid by ethyl alcohol in presence of hydrogen chloride and hydrogen bromide has been studied by Goldschmidt (*Abstr.*, 1896, i, 229) at a temperature of 25°. The results obtained at this temperature were so nearly alike that the conclusion was drawn that hydrogen chloride and hydrogen bromide are of equal efficiency under the conditions of the experiments. Goldschmidt and Sunde (*Abstr.*, 1906, ii, 219) and other authors have recorded physico-chemical measurements which seem to indicate that the efficiency of a catalytic agent depends on its concentration and its degree of dissociation in alcoholic solution.

In an investigation (this vol., i, 166) on the amount of ethyl benzoate formed from benzoic acid in presence of sulphuric acid, hydrogen chloride, or hydrogen chloride and zinc chloride as catalytic agents, with different quantities of alcohol acting for different lengths of time, it was found that the amount of ester produced was increased by increasing the concentration of the catalysts up to a certain limit, but that beyond this point the quantity was decreased. It was also found that the yields of ester did not bear any relation to the degree of ionisation of the catalyst. In the present paper, the catalytic action of hydrogen bromide alone and in presence of zinc bromide at different temperatures on the formation of ethyl benzoate is compared with that of hydrogen chloride and zinc chloride.

The results show that hydrogen bromide varies in its efficiency as a catalytic agent according to its concentration and the temperature at which esterification takes place. The amount of ethyl benzoate formed increases with the time of reaction. Zinc bromide also exerts a catalytic action. The greater the amount of either catalyst present, the greater is the yield of ester. It is found that esterification is retarded by raising the temperature above a certain point, and that a similar effect is produced when hydrogen chloride and zinc chloride are employed, but in this case only at such temperatures as are most unsuitable for esterification. The failure of zinc bromide to act efficiently at the higher temperatures is due to the action of hydrogen bromide on alcohol to form ethyl bromide and water. Hydrogen chloride is therefore more efficient than hydrogen bromide as a catalyst for esterification, although, as Goldschmidt has shown, at as low a temperature as 25°, they are of equal efficiency. The amount of ester produced is not proportional to the concentration of the hydrogen ions. Although, in all cases, the esterification proceeds more completely as the amount of the catalytic agent is increased up to a certain limit, any further increase causes a reduction in the quantity of ester produced. This seems to be due to the fact that all the catalysts employed have a strong affinity for water, and consequently, when they are present in large quantities, absolute alcohol is not able to effect dehydration as thoroughly as is necessary for complete esterification.

E. G.

Influence of Catalytic Agents in Ester Formation. Effect of Certain Sulphates on Benzoic and Succinic Acids. ISAAC K. PHELPS, H. E. PALMER, and R. SMILLIE (*Amer. J. Sci.*, 1908, [ix], 26, 290—295).—It has been shown previously (Abstr., 1907, i, 823; this vol., i, 166) that almost theoretical yields of ethyl succinate can be obtained by the action of hydrogen chloride and alcohol on succinic acid, and that quantitative yields of ethyl benzoate can be obtained from benzoic acid when sulphuric acid is used as a catalytic agent. Bogojawlensky and Narbutt (Abstr., 1905, i, 864) have investigated the influence of various inorganic sulphates on the esterification of certain organic acids.

In the present paper, the effect of the hydrogen sulphates of potassium, ammonium, sodium, pyridine, and aniline on the esterification of benzoic and succinic acids is recorded, and the results are compared with those obtained with sulphuric acid. It is found that none of these acid sulphates is so efficient as sulphuric acid. The sodium salt is nearly equal as a catalyst, the ammonium salt is less efficient, the potassium salt considerably less, whilst the pyridine and aniline salts are very poor catalysts. The pyridine salt is more efficient than the aniline salt in the esterification of succinic acid, but in the case of benzoic acid they produce nearly equal effects.

The catalytic action of these sulphates might be due to the dissociation of the sodium and potassium salts into the neutral sulphates and sulphuric acid, and of the pyridine and aniline sulphates into the free base and sulphuric acid, but this explanation fails in the case of the latter salts. Since, in most cases, the salt does not go into solution and an increase in the quantity of salt employed produces a marked effect, it is considered possible that the undissolved salts behave as contact agents. This question is being further investigated.

F. G.

Influence of Catalytic Agents in Ester Formation. Esterification of Benzoic Acid with Certain Chlorides. ISAAC K. PHELPS, M. A. PHELPS, and E. A. EDDY (*Amer. J. Sci.*, 1908, [iv], 26, 296—300).—The catalytic actions at 100—110° of the chlorides of sodium, potassium, lithium, ammonium, copper, calcium, strontium, barium, mercury, aluminium, manganese, tin, lead, antimony and bismuth in presence of small quantities of hydrogen chloride are compared with those of zinc chloride with hydrogen chloride and of hydrogen chloride alone.

The results show that zinc chloride is the most efficient, although copper and tin chlorides are not much less so. The higher chlorides of bismuth, antimony, and mercury are about equally efficient, and nearly as active as zinc, copper, and tin chlorides. Small quantities of calcium chloride are without effect, but large quantities hinder esterification to a marked extent. Strontium chloride retards the action to a smaller degree, and barium chloride hinders esterification but slightly. The chlorides of manganese and potassium, and the lower chlorides of lead and mercury, seem to be without effect. Sodium chloride hinders esterification slightly, lithium chloride more, ammonium chloride still

more, and aluminium chloride more than any of the chlorides studied, except calcium chloride when present in large quantities. E. G.

New Method of Preparing Mixed Organic Acid Anhydrides. J. BOUGAULT (*Compt. rend.*, 1908, 147, 249—251).—It has been shown previously (Abstr., 1905, i, 9; 1906, i, 848; this vol., i, 537) that an aqueous solution of sodium phenylisocrotonate (or generally the salt of any β -ethylenic acid) when treated with iodine gives an iodolactone, and that in the presence of a large excess of sodium carbonate the product consists of benzoylacrylic acid (this vol., i, 179, 269). It is now stated that if an aqueous solution of sodium phenylisocrotonate containing excess of sodium carbonate is treated with an equivalent quantity of an aromatic acid and then with iodine, the mixed anhydride of benzoylacrylic acid and the acid added is precipitated. In this manner the following anhydrides have been prepared: *Benzoylacrylic benzoic anhydride*, $\text{COPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{O}\cdot\text{COPh}$, slender colourless needles, m. p. 158° , which are not attacked by cold sodium carbonate solution, but are slowly acted on when heated on a water-bath with the alkali carbonate, acetophenone being evolved. Alkali hydroxide acts more rapidly. Addition of a small quantity of sodium carbonate solution to the boiling alcoholic solution of the anhydride causes the formation of ethyl benzoate. The anhydride is completely hydrolysed by fifteen minutes' boiling with 50% acetic acid. In the presence of zinc, the latter reaction gives benzoic and benzoylpropionic acids. *Benzoylacrylic cinnamic anhydride*, $\text{COPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{O}\cdot\text{CO}\cdot\text{CH}\cdot\text{CHPh}$, has m. p. 154° ; *benzoylacrylic phenylacetic anhydride*, $\text{COPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_2\text{Ph}$, m. p. 118° ; and *benzoylacrylic benzoylpropionic anhydride*, $\text{COPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{O}\cdot\text{CO}\cdot[\text{CH}_2]_2\cdot\text{COPh}$, m. p. 156° . The essential conditions of the reaction seem to be the insolubility of the anhydride and the nascent state of the benzoylacrylic acid.

The author points out that the exclusion of water and alkali, usually essential to the preparation of anhydrides, is unnecessary in this method. E. H.

Strength of the Second Stage [of the Dissociation] of Phenolcarboxylic and Phenolsulphonic Acids. ALFRED THIEL (*Zeitsch. anorg. Chem.*, 1908, 59, 371—372).—In reference to the observations of Ley and Erler (this vol., i, 177) and Obermüller (this vol., i, 634), it is pointed out that, whilst the approximation of the carboxyl group to the phenolic hydroxyl results in a diminution of the acidity of the latter group, the reverse holds good in reference to the influence of the sulphonic group on the acidity of phenolic hydroxyl. As a consequence of this relationship, the strength of the second stage of the hydrogen dissociation of *o*-phenolsulphonic acid is greater than that of *p*-phenolsulphonic acid. H. M. D.

Constitution of 1-Phenylnaphthalene-2:3-dicarboxylic Acid. JOHN E. BUCHER (*J. Amer. Chem. Soc.*, 1908, 30, 1244—1264).—Michael and Bucher (Abstr., 1898, i, 256) have shown that by the

action of acetic anhydride on phenylpropionic acid, 1-phenylnaphthalene-2:3-dicarboxylic anhydride is produced. This substance has also been studied by Lüsser (Abstr., 1899, i, 916), Mauthey (Abstr., 1901, i, 31), and Lüsser and Halvorsen (Abstr., 1902, i, 458). Stobbe (Abstr., 1907, i, 769) obtained the anhydride by the action of light on dibenzylidenesuccinic anhydride, and confirmed the constitution assigned to it by Michael and Bucher. In certain points, however, his conclusions differed from those of the latter authors, particularly with reference to the oxidation and reduction of the compound. A brief discussion of Stobbe's results has already been given (Michael and Bucher, this vol., i, 89). The results of a further study are now given in detail and confirm the previous work.

Stobbe (Abstr., 1907, i, 765) has stated that when 1-phenylnaphthalene-2:3-dicarboxylic acid is treated with concentrated sulphuric acid, a compound is produced which he termed *allochryso-ketonecarboxylic acid*. It is now shown that this compound is isomeric with 1-phenylnaphthalene-2:3-dicarboxylic acid, and has the constitu-

tion $\begin{matrix} \text{C}_6\text{H}_4 \\ \text{CO} \end{matrix} \rightarrow \text{C}_{10}\text{H}_8(\text{CO}_2\text{H})$; it melts at 288° without decomposition, and forms potassium and sodium salts containing water of crystallisation. On oxidation with potassium permanganate, it yields a yellow *diphenyleneketonetetracarboxylic acid*, $\begin{matrix} \text{C}_6\text{H}_4 \\ \text{CO} \end{matrix} \rightarrow \text{C}_6\text{H}(\text{CO}_2\text{H})_3$, and

when fused with potassium hydroxide is converted into a phenylnaphthalenedicarboxylic acid. The diphenyleneketonetetracarboxylic acid, on fusion with alkali hydroxide, yields a white *diphenyl-2:3:5:6-tetracarboxylic acid*, $\text{C}_6\text{H}_3(\text{CO}_2\text{H})_3 \cdot \text{C}_6\text{H}_4(\text{CO}_2\text{H})$, together with a small quantity of diphenyl-2:3:5:6-tetracarboxylic acid.

The action of acetic anhydride on piperonylpropionic acid, *o*-, *m*-, and *p*-chloro-, *o*- and *p*-bromo-, *m*- and *p*-nitro-, *p*-iodo-, and *p*-methoxyphenylpropionic acids has been studied. In each case an anhydride is produced which does not reduce alkaline permanganate solution, and is therefore a saturated compound, presumably a derivative of 1-phenylnaphthalene. The constitution of most of these compounds has been proved by transforming them into diphenyltetracarboxylic acid or by oxidising them to benzenepentacarboxylic acid.

*iso*Phthalic and terephthalic acids, when heated with acetic anhydride, are converted quantitatively into the corresponding *anhydrides*, which are almost insoluble in most organic solvents. E. G.

Esterification of Unsymmetrical Di- and Poly-basic Acids.
XVIII. Esterification of Dibasic Acids by Diazomethane.
RUDOLF WEGSCHEIDER and HEINRICH GEHRINGER (*Monatsh.*, 1908, 29, 525—530. Compare Abstr., 1907, i, 850).—The acid (2 mols.) and diazomethane (1 mol.) react in ether. The main products are usually the normal ester and unchanged acid; in addition to these, 3-nitrophthalic acid, hemipinic acid, and nitroterephthalic acid yield small quantities of the α -methyl ester, whilst 4-hydroxyphthalic acid and camphoric acid give mixtures of the two acid esters. The method is unsuitable for the production of acid esters. C. S.

Esterification of Unsymmetrical Di- and Poly-basic Acids.
XIX. Esterification of Phthalonic Acid. RUDOLF WEGSCHEIDER (*Monatsh.*, 1908, 29, 531—534).—A theoretical discussion of the partial esterification of phthalonic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CO}_2\text{H}$, showing that the aliphatic carboxyl group, being the more strongly acidic, should be first esterified, a result which has been already established by Glogau (*Abstr.*, 1904, i, 673). C. S.

Esterification of Unsymmetrical Di- and Poly-basic Acids.
XX. Methyl Esters of 3-Nitrophthalic Acid. RUDOLF WEGSCHEIDER (*Monatsh.*, 1908, 29, 535—539).—The m. p. of the α -methyl ester of 3-nitrophthalic acid ($\text{CO}_2\text{Me}:2$), dried at 100° , is given by different investigators as $144\text{—}145^\circ$ or $152\text{—}153^\circ$ (compare McKenzie, *Trans.*, 1901, 79, 1141). The suggestion of decomposition during dehydration is negated by the fact that, after being maintained at 100° for 363 hours, the ester has practically the same m. p. as after fifteen hours' heating. Rapidity of heating in the m. p. determination or the existence of mixed crystals of the α and the β methyl esters is not the explanation of the difference. The author suggests the possibility of polymorphism, but satisfactory evidence of it was not obtainable.

The α methyl ester, m. p. $149\text{—}151^\circ$, forms short, monoclinic prisms containing H_2O [$a:b:c=0.5883:1:0.6731$]. The β ester ($\text{CO}_2\text{Me}:1$) forms anhydrous, monoclinic crystals [$a:b:c=0.2678:1:0.2260$].

C. S.

Esterification of Unsymmetrical Di- and Poly-basic Acids.
XXI. Nitrohemipinic Acid. RUDOLF WEGSCHEIDER and PETER VON RUŠNOV (*Monatsh.*, 1908, 29, 541—555).—Of the two carboxyl groups in hemipinic acid (3:4-dimethoxybenzene-1:2-dicarboxylic acid), that in position 2 is the more strongly acidic and the more subject to steric hindrance. By nitration, a nitro-group enters position 6, and in the resulting nitrohemipinic acid the two preceding characteristics are more pronounced in the carboxyl group in position 1, owing to the influence of the nitro-group. Partial esterification of the two acids by the same method gives, accordingly, acid esters in which different carboxyl groups have been attacked. Both acids yield chiefly the α methyl ester by the action of methyl alcohol on the anhydrides or from methyl iodide and the potassium hydrogen salts, whilst the β ester is the chief product of esterification by an alcohol and mineral acid. (In accordance with the authors' notation, the more strongly acidic carboxyl group is denoted by α ; this prefix, therefore, designates different carboxyl groups in the two acids in question.) The neutral esters of the two acids behave differently on partial hydrolysis; whilst dimethyl hemipinate yields entirely the α methyl ester, the neutral ester of 6-nitrohemipinic acid, which, contrary to expectation, is obtained without much difficulty by methyl-alcoholic hydrogen chloride, gives about equal quantities of the α and the β esters. Similarly, hemipinic acid and methyl alcohol at 100° give the α ester, whilst nitrohemipinic acid heated with methyl alcohol in an open vessel gives both α and β esters, the latter in larger amount.

[With LEO KUSY VON DÜBRAY.]—6-Nitrohemipinic acid, m. p.

155—156° (decomp.), is obtained by oxidising nitro-opianic acid by hot dilute, alkaline potassium permanganate, or, better, by nitrating hemipinic acid in glacial acetic acid at 90—100° by fuming nitric acid. *α*-Methyl 6-nitrohemipinate ($\text{CO}_2\text{Me}:1$) has m. p. 147—149°, and can also be obtained by nitrating *δ*-methyl hemipinate. *δ*-Methyl 6-nitrohemipinate ($\text{CO}_2\text{Me}:2$) has m. p. 115—117°.

Nitration of *α*-methyl hemipinate gives a substance, m. p. 142—144°, not identical with, but of the same composition as, *α*- or *δ*-methyl nitrohemipinate. The substance, which is being investigated, is apparently a ψ -ester, $\text{NO}_2\cdot\text{C}_6\text{H}(\text{OMe})_2 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{C}(\text{OH})(\text{OMe}) \end{array} \text{O}$, since it yields nitrohemipinic acid by hydrolysis.

C. S.

Esterification of Unsymmetrical Di- and Poly-basic Acids.
XXII. Isomerism of Methyl Nitrohemipinates. RUDOLF WEGSCHEIDER and HUGO STRAUCH (*Monatsh.*, 1908, 29, 557—572).— ψ -Methyl 6-nitrohemipinate, m. p. 142—144° (preceding abstract), can also be obtained by nitrating either of the polymorphous forms of *α*-methyl hemipinate at 0° without a solvent. A by-product, which becomes the main product when the nitration is performed at 30—50°, is methyl dinitrodimethoxybenzoate, m. p. 89—90°, the orientation of which is being investigated.

That the ψ -ester is a derivative of 6-nitrohemipinic acid is proved by hydrolysis, the resulting acid being identical with this acid in all respects. (6-Nitrohemipinic anhydride, obtained by heating the acid at 160—165° in carbon dioxide, has m. p. 155°, not 145° as usually given.) The remarkable fact that 6-nitrohemipinic acid forms three acid methyl esters cannot be explained by polymorphism, since the three esters are precipitated unchanged by acidification of their solutions in alkalis. Experiments for the mutual interconversion of the esters have been unsuccessful. The author revives the old speculation of Roser and Anschütz that dicarboxylic acids may exist in the forms $\text{R}(\text{CO}_2\text{H})_2$ and $\text{R} \begin{array}{c} \text{C}(\text{OH})_2 \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{O}$. This theory, unnecessary in the case

of the great majority of dicarboxylic acids, may serve to account for the occasional abnormally small affinity constants of some dibasic acids and acid esters, and is applicable to opianic and hemipinic acids. The former shows the conductivity of an aldehyde-acid, and yields both normal and ψ -esters. Nitro-opianic acid and its ester exist in the ψ -forms. The nearly related hemipinic acid shows no tendency to exist in the ψ -form. The introduction of the nitro-group, however, increases its tendency to the latter form, so that, whilst nitrohemipinic acid itself has the normal structure, it is capable of yielding a stable ψ -acid ester, $\text{NO}_2\cdot\text{C}_6\text{H}(\text{OMe})_2 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{C}(\text{OH})(\text{OMe}) \end{array} \text{O}$.

C. S.

Synthesis of Some Aromatic Acids. JOHAN F. EYKMAN (*Chem. Weekblad*, 1908, 5, 655—666. Compare this vol., i, 22).—A continuation of the author's work on the synthesis of aromatic acids by the action of aromatic hydrocarbons on unsaturated acids in presence of aluminium chloride. Most of the reactions were

carried out by maintaining the mixtures at 30° for about four weeks.

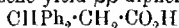
β -Phenyl-*n*-butyric acid, $\text{CHPhMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (Schroeter, Abstr., 1907, i, 531), is obtained from crotonic acid and benzene; it has b. p. 140–145°/3 mm. It crystallises from light petroleum in monoclinic, columnar crystals [$\alpha:\beta:\gamma=1.22:1.108$; $\beta=90.52^\circ$], m. p. 37–38° (Schroeter: 39–40°). The *amide* forms colourless needles, m. p. 106–107°. The *anilide* has m. p. 136–137°. The refractive-index constants of the acid are given. Toluene does not yield a similar condensation product with crotonic acid.

α -Phenyl- β -methylbutyric acid, $\text{CHMe}_2\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$, is obtained from $\beta\beta$ -dimethylacrylic acid and benzene. It separates from light petroleum in large crystals, m. p. 58–59° (freezing point, 57.4°). The constitution indicated is supported by the fact that the sodium salt has no action on benzaldehyde in presence of either acetic anhydride or the acid chloride, which points to the absence of the group $-\text{CH}_2\cdot\text{CO}_2\text{H}$, and therefore excludes the alternative formula $\text{CPhMe}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$. The *amide* has m. p. 68°; the *anilide* 121°. Nitric acid yields a crystalline nitro-acid, m. p. 175° (from alcohol). With toluene, $\beta\beta$ -dimethylacrylic acid yields an *acid*, b. p. 178°/21 mm., which has not been obtained crystalline.

A phenylhydrotiglic acid is formed from tiglic acid and benzene. Crystallised from a mixture of benzene and light petroleum, it has m. p. 132°. Its constitution has not been established, but it may be α -phenyl- α -methylbutyric acid, $\text{CPhMeEt}\cdot\text{CO}_2\text{H}$.

$\alpha\alpha$ -Diphenylacetic acid, $\text{CHPh}_2\cdot\text{CO}_2\text{H}$ (compare Symons and Zincke, this Journ., 1874, 162; Friedel and Bahlsohn, Abstr., 1881, 273; Anschütz and Romig, Abstr., 1886, 1033; Zinzer, Abstr., 1892, 344; Michael and Jeanprêtre, Abstr., 1892, 1088; Klingemann, Abstr., 1893, i, 590; Fritsch and Feldmann, Abstr., 1899, i, 600), is formed from $\alpha\alpha$ -bromophenylacetic acid and benzene. It separates from a mixture of benzene and light petroleum in crystals, m. p. 148–149°.

Cinnamic acid and benzene yield $\beta\beta$ -diphenylpropionic acid,



(Henderson, Trans., 1891, 784; Liebermann and Hartmann, Abstr., 1892, 848, 1223), which crystallises from benzene, m. p. 154–155° (corr.). The oxidation of the acid by permanganate to benzophenone, and its formation from $\beta\beta$ -bromophenylpropionic acid, establish its constitution. The *amide* crystallises from benzene in glistening leaflets, m. p. 125–126°; the *anilide* from alcohol, m. p. 177–178°.

$\alpha\alpha$ -Diphenylpropionic acid, $\text{CPh}_2\text{Me}\cdot\text{CO}_2\text{H}$ (Thörner and Zincke, Abstr., 1873, 322; Böttiger, Abstr., 1881, 1035), is formed from α -phenylacrylic acid and benzene. It separates from benzene in crystals, m. p. 173–174°. α -Phenylcrotonic acid does not condense with benzene in presence of aluminium chloride.

$\beta\beta$ -Diphenyl- α -methylpropionic acid, $\text{CHPh}_2\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, is prepared from α -methylcinnamic acid and benzene, and separates from benzene in crystals, m. p. 161°. Permanganate oxidises it to benzophenone. The *amide* has m. p. 123°; the *anilide* 181°. The *methyl*

ester is obtained by saturating a solution of the acid in methyl alcohol with hydrogen chloride. After distillation in a vacuum and recrystallisation from light petroleum, it has m. p. 84—85°.

α -Ethylcinnamic acid and benzene yield an acid, which from analogy to that obtained from the corresponding methyl derivative is probably $\beta\beta$ -diphenyl- α -ethylpropionic acid, $\text{CHPh}_2\cdot\text{CHEt}\cdot\text{CO}_2\text{H}$. Crystallised from benzene, it has m. p. 167—168°. The amide has m. p. 150°; the anilide 211°.

$\alpha\beta\beta$ -Triphenylpropionic acid, $\text{CHPh}_2\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$, is obtained from α -phenylcinnamic acid and benzene. It is freed from a yellow by-product by dissolving in alcohol and saturating with hydrogen chloride. On diluting with water, the bulk of the acid separates unchanged, along with a small proportion of the ethyl ester. The mixture is agitated with dilute caustic alkali, the alcoholic solution extracted with ether, and acidified. The pure acid separates in fine, white needles, m. p. 222—223°. After distillation in a vacuum and recrystallisation from alcohol, the ester is obtained in glistening leaflets, m. p. 122—123°.

A. J. W.

Oxidation and Reduction of γ -Cyano- $\beta\gamma$ -diphenylbutyric Acid. SAMUEL AVERY and GUY R. McDOLLE (*J. Amer. Chem. Soc.*, 1908, 30, 1423—1425. Compare this vol., i, 343).—Additional evidence of the correctness of the constitution of γ -cyano- $\beta\gamma$ -diphenylbutyric acid is afforded by its behaviour on oxidation and reduction. When the acid is oxidised with neutral potassium permanganate, desylacetic acid, $\text{CHPhBz}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, is obtained, whilst, on reduction with hot sodium ethoxide and subsequent addition of hydrochloric acid, a mixture of $\beta\gamma$ -diphenylbutyric acid and the hydrochloride of δ -amino- $\beta\gamma$ -diphenylvaleric acid, white, blunt needles, m. p. 256°, is formed.

J. C. C.

Nitration of β -*p*-Tolylglutaric Acid. SAMUEL AVERY and FRED W. UPSON (*J. Amer. Chem. Soc.*, 1908, 30, 1425—1429).—When β -*p*-tolylglutaric acid (Avery and Parmelee, *Abstr.*, 1902, i, 679) is added to ten times its weight of fuming nitric acid, 3 : 5-dinitro- β -*p*-tolylglutaric acid, pale yellow, microscopic plates, m. p. 182°, is obtained. The anhydride, hard, white, glistening plates, has m. p. 230—231°, and gives with aniline the anilic acid, white, microscopic needles, m. p. 169—170°. On reduction with ammonium sulphide, the glutaric acid furnishes 3-nitro-5-amino- β -*p*-tolylglutaric acid, yellowish-brown needles, m. p. 201°, the silver salt of which was analysed, and, on oxidation, 3 : 5-dinitroterephthalic acid is formed. The constitution of 3 : 5-dinitro- β -*p*-tolylglutaric acid was proved by the following synthesis: methyl *m*-nitro-*p*-tolylacrylate (Hanzlik and Bianchi, *Abstr.*, 1899, i, 891) is condensed with ethyl malovate, and the product hydrolysed to 3-nitro- β -*p*-tolylglutaric acid, m. p. 198.5°. On nitration this yields a dinitro-acid identical with the above.

J. C. C.

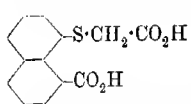
Fixation of Acetophenone by Benzoylacrylic Acid. J. BOUCAULT (*Compt. rend.*, 1908, 147, 476—478. Compare this vol., i, 179, 269, 422).—When an alkaline solution of benzoylacrylic acid is

allowed to remain in the cold for twenty-four hours and then acidified with acetic acid, diphenacylacetic acid is obtained. As von Pechmann found (Abstr., 1882, 1074) that boiling alkalis decompose benzoylacrylic acid with the formation of glyoxylic acid and acetophenone, it is probable that the same reaction proceeds more slowly in the cold, and that the acetophenone formed combines with still undecomposed benzoylacrylic acid in equimolecular proportions. This is proved to be the case by adding acetophenone to an alkaline solution of benzoylacrylic acid, when an increased yield of diphenacylacetic acid, $(\text{CH}_2\text{Bz})_2\text{CH}\cdot\text{CO}_2\text{H}$, is invariably obtained. J. C. C.

Preparation of Alkylthiosalicylic [2-Alkylthiolbenzoic] Acids. FARBERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 197520).—When *o*-thiocyanobenzoic acid and its derivatives are treated either with alkyl iodides or alkali alkyl sulphates, they yield *o*-alkylthiolbenzoic acids of the general formula $\text{R}(\text{S}\cdot\text{Alkyl})\cdot\text{CO}_2\text{H}$.

o-Methylthiolbenzoic acid, $\text{C}_6\text{H}_4(\text{SMe})\cdot\text{CO}_2\text{H}$, m. p. 168—169°, is obtained by heating together in aqueous sodium hydroxide, *o*-thiocyanobenzoic acid and sodium methylsulphate. *o*-Ethylthiolbenzoic acid, $\text{C}_6\text{H}_4(\text{SEt})\cdot\text{CO}_2\text{H}$, m. p. 134—135°, is produced from *o*-thiocyanobenzoic acid, ethyl iodide, and potassium hydroxide in alcoholic solutions; the *ethyl* ester which is first formed is an oil, b. p. 152—153°/10 mm. G. T. M.

[Preparation of 8-Carboxymethylthiolnaphthoic Acid.] FARBERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 198050).—



8-Carboxymethylthiolnaphthoic acid, colourless leaflets, m. p. 175—176°, is prepared by treating the diazo-derivative of 8-aminonaphthoic acid successively with potassium xanthate and sodium chloroacetate. Blue colouring matters are produced by heating this substance with aqueous alkali hydroxides, nitrobenzene, acetic anhydride, acid sulphites, thiosulphates, or sulphur; these dyes are suitable for the hyposulphite vat (compare this vol., i, 451, and preceding abstract). G. T. M.

Preparation of 3-Hydroxy-(1)-thionaphthen-2-carboxylic Acid. KALLE and Co. (D.R.-P. 196016. Compare this vol., i, 451).

—A good yield of 3-hydroxy-(1)-thionaphthen-2-carboxylic acid is obtained by heating at 150—200° a mixture of phenylthioglycol-*o*-carboxylic (*o*-carboxymethylthiobenzoic) acid and sodium hydroxide, and acidifying the product at the ordinary temperature. If the mixture becomes heated, carbon dioxide is evolved, and 3-hydroxy-(1)-thionaphthen is produced. G. T. M.

Preparation of Indoxyl and its Derivatives. LEON LILIENFELD (D.R.-P. 195352).—Comparative experiments on Heumann's indigo synthesis have shown that the addition of magnesium powder to the alkali fusion of phenylglycine and its homologues considerably increases the yield of indigotin. Thus a mixture of potassium phenylglycine, sodium and potassium hydroxides, and barium oxide furnished

only 27% of indigotin, whereas the addition of magnesium raised the yield to 60%.

G. T. M.

Preparation of Tri-, Tetra-, and Hexa-halogenated Derivatives of Indigotin. GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 195085 and 195291. Compare this vol., i, 695).—*Chlorodibromoindigotin*, $C_{16}H_2O_2N_2ClBr_2$, is obtained by heating chloroindigotin with bromine in nitrobenzene at 226–228°. With a larger proportion of bromine, a chlorotribromoindigotin, $C_{16}H_2O_2N_2ClBr_3$, is produced. These products give leuco-derivatives in the hyposulphite vat, which dye cotton in bright blue shades of extraordinary fastness. *p*-Dichloroindigotin, prepared from 4-chloro-2-aminobenzoic acid, when heated at 225° with bromine in nitrobenzene solution, gives rise to a *dichlorotetrabromoindigotin*, which yields a yellow leuco-derivative. When *p*-dibromoindigotin is employed in this reaction, *hexabromoindigotin* is obtained.

G. T. M.

Preparation of Succinylsalicylic Acid and its Methyl Homologues. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.P. 196634).—*Succinylsalicylic acid*, $C_2H_4(CO \cdot O \cdot C_6H_4 \cdot CO_2H)_2$, white, tasteless, colourless needles, m. p. 176–178°, produced by the interaction of succinyl chloride, salicylic acid, and dimethylaniline in benzene solution, dissolves very sparingly in water, and is only slightly soluble in cold alcohol or glacial acetic acid.

Succinyl-o-cresotic acid, $C_2H_4(CO \cdot O \cdot C_6H_3Me \cdot CO_2H)_2$, tasteless, crystalline powder, m. p. 163–164°. *Succinyl-m-cresotic acid*, m. p. 195–197°, and *succinyl-p-cresotic acid*, colourless crystals, m. p. 193–195°, are prepared by the foregoing reaction, and resemble the preceding compound.

G. T. M.

Arylsulphonated Acetonitriles. II. Condensation of the Nitriles with Aromatic Aldehydes and with Amyl Nitrite and Sodium Ethoxide. JULIUS TROGER and ADOLF PROCHNOW (*J. pr. Chem.*, 1908, [iii], 78, 123–138).—The similarity between arylsulphonated acetonitriles (Abstr., 1905, i, 336, 870; this vol., i, 633), on the one hand, and ethyl acetoacetate, ethyl cyanoacetate, or benzyl cyanide, on the other, is further illustrated by the readiness with which the nitriles condense with aromatic aldehydes and with amyl nitrite and sodium ethoxide. The RSO_2 group in combination with a nitrile group has much the same effect on the methylene group as carbonyl and carboxy radicals. The condensation with aldehydes takes place readily in the presence of a few drops of aqueous sodium hydroxide; the reaction is of the type $R \cdot CH \cdot O + R' SO_2 \cdot CH_2 \cdot CN \rightarrow R \cdot CH \cdot C(SO_2 R') \cdot CN + H_2O$. The following condensation products (arylsulphonarylideneacetonitriles) have been prepared. The temperatures are melting points:

$R = R' = Ph$, colourless needles, 135°; $R = o-C_6H_4 \cdot OH$, $R' = Ph$, microcrystalline needles, 160°; $R = o-C_6H_4 \cdot OMe$, $R' = Ph$, yellow needles, 113°; $R = p-C_6H_4 \cdot NO_2$, $R' = Ph$, yellow needles, 159°; $R = C_6H_5$, $R' = CH_3$, $R' = Ph$, yellow needles, 146°; $R = Ph$, $R' = p-C_6H_4 \cdot Me$, colourless needles, 114°; $R = o-C_6H_4 \cdot OH$, $R' = p-C_6H_4 \cdot Me$, 152°; $R = o-C_6H_4 \cdot OMe$, $R' = p-C_6H_4 \cdot Me$, yellow needles, 110°; $R = p-C_6H_4 \cdot NO_2$, $R' = p-C_6H_4 \cdot Me$

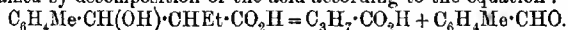
yellow needles, 198°; R=Ph, R'=β-C₁₀H₇, 122°; R=o-C₆H₄·OH, R'=β-C₁₀H₇, microcrystalline needles, 173°; R=o-C₆H₄·OMe, R'=β-C₁₀H₇, pale yellow needles, 117°; R=p-C₆H₄·NO₂, R'=β-C₁₀H₇, yellow needles, 187°; R=C₆H₅·CH:CH, R'=β-C₁₀H₇, yellow needles, 157°; R=Ph, R'=p-C₆H₄Br, large needles, 119°; R=o-C₆H₄·OH, R'=p-C₆H₄Br, needles, 143°; R=o-C₆H₄·OMe, R'=p-C₆H₄Br, yellow needles, 146°; R=p-C₆H₄·NO₂, R'=p-C₆H₄Br, yellow needles, 210°; R=C₆H₅·CH:CH, R'=p-C₆H₄Br, yellow needles, 176°.

The condensation between the arylsulphonated nitriles, amyl nitrite, and sodium ethoxide may be represented by the equation $C_5H_{11}ONO + RSO_2 \cdot CH_2 \cdot CN + NaOEt \rightarrow C_5H_{11}OH + EtOH + NaO \cdot N \cdot C(SO_2R)CN$, the methylene hydrogen atoms being replaced by the bivalent oxime group. The free oximes are obtained when the sodium salts are decomposed with hydrochloric acid. The following oximes (isonitroso-compounds) have been prepared: R=Ph, colourless crystals from water, 140°; R=p-C₆H₄Me, colourless crystals, 129°; R=β-C₁₀H₇, 80°; R=p-C₆H₄Br, 163°.

J. J. S.

Synthesis and Properties of β-Hydroxy-β-m-tolyl-α-ethylpropionic Acid. E. GRISHKEWITSCH-TROCHIMOWSKY (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 761—769).—Ethyl β-hydroxy-β-m-tolyl-α-ethylpropionate, C₆H₄Me·CH(OH)·CHEt·CO₂Et, prepared by the action of zinc on a mixture of ethyl α-bromobutyrate and m-tolualdehyde, is a viscous, colourless liquid, b. p. 187.5—188°/31 mm., and has the normal molecular weight in boiling ether or freezing benzene.

The acid, C₆H₄Me·CH(OH)·CHEt·CO₂H, separates from water in colourless, acicular crystals, m. p. 109.5—110°, and exhibits normal bullisoscopic behaviour in ether. When boiled with 10% sulphuric acid, the acid decomposes in two ways: (1) giving CO₂, H₂O and α-m-tolyl-Δ³-butylene, C₆H₄Me·CH:CHEt, which is a colourless, mobile liquid, b. p. 208°, D₁₅²⁰ 0.8901, n_D²⁰ 1.5365, and forms the dibromide, C₁₁H₁₄Br₂; (2) giving m-toluic acid, which probably results from m-tolualdehyde obtained by decomposition of the acid according to the equation:

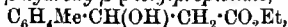


The potassium, C₁₂H₁₅O₃K, H₂O, barium, (C₁₂H₁₅O₃)₂Ba, 8H₂O, copper, silver, C₁₂H₁₅O₃Ag, iron, lead, zinc, and platinum salts of the acid were prepared.

The properties of the acid are compared with those of β-hydroxy-3-p-tolyl-α-ethylpropionic acid (compare Mazurewitsch, Abstr., 1907, 623).

T. H. P.

Action of a Mixture of Ethyl Bromoacetate and p-Tolualdehyde on Zinc. Synthesis of β-Hydroxy-β-p-tolylpropionic Acid. W. ANDRIEWSKY (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 170—172).—Ethyl β-hydroxy-β-p-tolylpropionate,



obtained by the action of zinc on a mixture of ethyl bromoacetate and p-tolualdehyde, is a yellow, viscous liquid, b. p. 178—180°/19 mm.

The corresponding acid, C₆H₄Me·CH(OH)·CH₂·CO₂H, separates from aqueous alcohol in acicular crystals, m. p. 94—95°, and has the normal molecular weight in boiling ether. The potassium, silver, and

barium (+ 2H₂O) salts were analysed, and the ammonium, mercury, zinc, copper, iron, lead, and nickel salts prepared.

When boiled with 10% sulphuric acid solution, the acid is decomposed mainly in accordance with the equation:

$C_6H_4Me \cdot CH(OH) \cdot CH_2 \cdot CO_2H = H_2O + C_6H_4Me \cdot CH:CH \cdot CO_2H$,
yielding *p*-methylcinnamic acid, a small part of which undergoes further decomposition with formation of *p*-methylstyrene,
 $C_6H_4Me \cdot CH:CH_2$,

and carbon dioxide. When subjected to dry distillation at 130°, the acid decomposes into water and *p*-methylcinnamic acid (compare Bronstein, Abstr., 1907, i, 848).
T. H. P.

Preparation of Aromatic o-Hydroxyaldehydes. HUGO WEIL (D.R.-P. 196239).—A solution of a salicylate when shaken with sodium amalgam shows no apparent change, but when boric acid is first added, the introduction of the amalgam develops immediately an odour of salicylaldehyde.

When *p*-toluidine is also present, *o*-hydroxybenzylidene-*p*-toluidine is produced. The reduction may be carried out electrolytically by using a mercury cathode and a solution containing a sodium salt.
G. T. M.

Derivatives of Phenyl α -Naphthyl Ketone. E. CAILLÉ (Bull. Soc. chim., 1908, [iv], 3, 916—919).—When an alcoholic solution of phenyl α -naphthyl ketone is treated with sodium amalgam, it yields *phenyl- α -naphthylcarbinol*, which crystallises from alcohol in white, orthorhombic prisms, m. p. 85°, and gives a violet coloration with sulphuric acid; the *benzoyl* derivative, m. p. 106°, crystallises from alcohol in colourless plates, giving a violet coloration with sulphuric acid. The oxime of phenyl α -naphthyl ketone, described by Spiegler (Abstr., 1884, 1182) as a yellow oil, when prepared by the action of hydroxylamine on the ketone, with the addition of zinc chloride, forms white, silky needles, m. p. 73°, and gives an orange coloration with sulphuric acid. The *phenylhydrazone*, m. p. 189°, forms a yellow mass, which reddens on exposure to air and gives a green coloration with sulphuric acid.
J. C. C.

Formation of Oximes. UGO GRASSI (Gazzetta, 1908, 38, ii, 32—40).—The formation of *l*-menthoneoxime from *l*-menthone and free hydroxylamine is accelerated by raising the temperature and also by increasing the proportion of alcohol in the solution. In some cases, the optical activity of the solution diminishes considerably instead of increasing, as it should do were the oxime formed. This cannot be due to inversion of the menthone, since the solutions employed were quite neutral to litmus and phenolphthalein, and the proportion of alcohol present was too small to produce rapid inversion. The author therefore assumes the formation of an intermediate compound, which is probably a simple additive compound, $OH \cdot CRR' \cdot O \cdot NH_2$, analogous to those formed by the hydrogen sulphites, or by ammonia with aldehydes, and stable at low temperatures. This compound then passes into the oxime by a process of dehydration, which may well be

accelerated by rise of temperature or by alcohol. Some of the solutions of *l*-menthone and hydroxylamine were found to attain a final rotation higher than that calculated for the oxime from the values given by Beckmann (Abstr., 1889, 721).

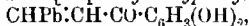
With regard to the acceleration of the formation of oximes by dehydrating agents, it is found that camphoroxime is formed much more rapidly in absolute alcohol containing anhydrous sodium sulphate than in absolute alcohol alone.

The distribution of hydroxylamine between two ketones has been studied in 94% alcohol at 35°. Under these conditions, hydroxylamine combines with acetone in preference to menthone, but acetone in large excess is unable to remove hydroxylamine from menthoneoxime, at any rate in neutral solutions. Even oximes, such as that of pinacol, which Stewart's investigations (Trans., 1905, 87, 185, 410) show to be the weakest, resist energetically the action of other ketones.

T. H. P.

2':4'-Dihydroxyhydrochalkone. GUIDO BARGELLINI and M. MARANTONIO (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 119—125).—**2':4'-Dihydroxyhydrochalkone** [*o*:*p*-dihydroxyphenyl phenylethyl ketone], $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_3(\text{OH})_2$, prepared by the condensation of hydrocinnamic acid and resorcinol in presence of zinc chloride, crystallises from dilute acetic acid in needles, m. p. 88°, dissolves in alkali hydroxide solutions or in concentrated sulphuric acid, giving pale yellow solutions, and in aqueous solution gives a yellow coloration with ferric chloride. The acetyl derivative was obtained as a pale yellow resin which could not be purified. The monomethyl ether, $\text{C}_{16}\text{H}_{16}\text{O}_3$, crystallises from water in white needles, m. p. 74—75°, and the dimethyl ether, $\text{C}_{17}\text{H}_{18}\text{O}_3$, from dilute acetic acid in long needles, m. p. 103—104°. The oxime, $\text{C}_{17}\text{H}_{18}\text{O}_3\text{N}$, crystallises from benzene as a white powder, m. p. 171—172°. The ketone is not attacked when heated for several hours with 70% potassium hydroxide solution (compare Weisl, Abstr., 1905, i, 904; Finzi, Abstr., 1905, i, 906).

2':4'-Dihydroxychalkone [*o*:*p*-dihydroxyphenyl styryl ketone],



prepared by the condensation of cinnamic acid and resorcinol in presence of zinc chloride, crystallises from water in needles, m. p. 175°.

T. H. P.

Coloured Hydrohalides of Unsaturated Aromatic Ketones.

LUIGI FRANCESCONI and G. CUSMANO (*Gazzetta*, 1908, 38, ii, 70—97).

—The authors have prepared a number of aromatic ketones containing various substituent groups and from one to four double linkings in different positions with respect to the carbonyl group. The ketones have been subjected to the action of dry hydrogen chloride, the derivatives obtained being unstable towards water (compare Baeyer and Villiger, Abstr., 1901, i, 659; 1902, i, 355; Vorländer and Mumme, Abstr., 1903, i, 495; Straus and Ecker, Abstr., 1906, i, 859). Certain of the ketones containing three double linkings have been treated with bromine, the addition of which is only partial in some

cases and total in others; the behaviour of some of these bromo-derivatives towards hydrogen chloride has been studied.

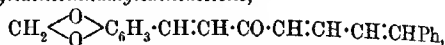
Methylvanillylideneacetone, $\text{CH}_3 \cdot \text{CO} \cdot \text{CH} : \text{CH} \cdot \text{C}_6\text{H}_3(\text{OMe})_2$, prepared by the interaction of methylvanillin and aqueous acetone in presence of sodium hydroxide or by methylating vanillylideneacetone, crystallises from ethyl acetate in yellow needles, m. p. 168°.

Benzylidenecinnamylideneacetone (compare Scholtz, Abstr., 1896, i, 368) has m. p. 109—110°.

Anisylidenecinnamylideneacetone,

$\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} \cdot \text{CO} \cdot \text{CH} : \text{CH} \cdot \text{CH} : \text{CHPh}$, separates from a mixture of ether and ethyl acetate in pale yellow crystals, m. p. 138°.

Piperonylidene-cinnamylideneacetone,



is deposited from ethyl acetate in shining, pale yellow crystals, m. p. 127°.

Methylvanillylidene-cinnamylideneacetone,

$\text{C}_6\text{H}_3(\text{OMe})_2 \cdot \text{CH} : \text{CH} \cdot \text{CO} \cdot \text{CH} : \text{CH} \cdot \text{CH} : \text{CHPh}$, crystallises from ether in pale yellow leaflets, m. p. 110°.

Salicylidene-cinnamylideneacetone,

$\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} \cdot \text{CO} \cdot \text{CH} : \text{CH} \cdot \text{CH} : \text{CHPh}$ (?), obtained by condensing salicylaldehyde with cinnamylideneacetone in presence of sodium hydroxide, crystallises from chloroform in pale yellow leaflets, m. p. 163°.

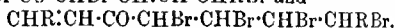
Vanillylidene-cinnamylideneacetone,

$\text{OH} \cdot \text{C}_6\text{H}_3(\text{OMe}) \cdot \text{CH} : \text{CH} \cdot \text{CO} \cdot \text{CH} : \text{CH} \cdot \text{CH} : \text{CHPh}$ (?), obtained only in small quantity, is a pale yellow compound.

It would be expected that ketones of the type



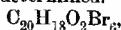
would yield two dibromides, $\text{CHBr} \cdot \text{CHBr} \cdot \text{CO} \cdot \text{CH} : \text{CH} \cdot \text{CH} : \text{CHR}$ and $\text{CHR} : \text{CH} \cdot \text{CO} \cdot \text{CHBr} \cdot \text{CH} : \text{CH} \cdot \text{CHBr}$, and two tetrabromides, $\text{CHBr} \cdot \text{CHBr} \cdot \text{CO} \cdot \text{CHBr} \cdot \text{CH} : \text{CH} \cdot \text{CHBr} \cdot \text{CHBr}$ and



By the action of two or four atoms of bromine on anisylidenecinnamylideneacetone or piperonylidene-cinnamylideneacetone, however, only one di- or tetra-bromide could be isolated. Like the unsaturated aromatic ketones themselves, the dibromides and monohydrobromides of ketones of the type of dibenzylideneacetone give colorations with concentrated sulphuric acid, but no coloration is given by the coloured tetrabromides or dihydrobromides. A coloration is hence only obtained when an ethylene linking is present, and when it is next to the double linking of the carbonyl group. From their ability or inability to give a coloration with sulphuric acid, it is therefore possible to decide the constitution of the tetrahalogenated derivatives, and, since these, with one exception, give no coloration, they must have the structure $\text{CHBr} \cdot \text{CHBr} \cdot \text{CO} \cdot \text{CHBr} \cdot \text{CH} : \text{CH} \cdot \text{CHBr} \cdot \text{CHBr}$; dibromides of either of the constitutions given above would give a coloration with sulphuric acid, so that in their case the structure cannot be settled.

Anisylidenecinnamylideneacetone dibromide, $\text{C}_{20}\text{H}_{18}\text{O}_2\text{Br}_2$, m. p. 135—136° (decomp.), does not increase in weight or become coloured in

contact with dry hydrogen chloride, but gives a peacock-blue coloration with concentrated sulphuric acid. The *tetrabromide*, $C_{20}H_{18}O_2Br_4$, m. p. 146–147°, which gradually gives a violet coloration with sulphuric acid, was obtained together with another compound, m. p. 131–133°, the nature of which was not determined. The *hexabromide*,



separating from ether as a white, microcrystalline powder, m. p. 144°, and gradually giving a violet coloration with sulphuric acid, was obtained together with a whitish-violet, microcrystalline powder, m. p. 172.5°.

Piperonylideneinnamylideneacetone dibromide, $C_{20}H_{18}O_2Br_2$, separates from chloroform in faintly yellow, microscopic crystals, m. p. 149–150°, and gives an intense coloration with sulphuric acid, but is not affected by hydrogen chloride. The *tetrabromide*, $C_{20}H_{18}O_2Br_4$, m. p. 147–148°, obtained as a white powder becoming faintly rose-red in the light, gives no coloration with either sulphuric acid or hydrogen chloride. The hexabromide could not be prepared, an unsaturated compound derived from the hexabromide by elimination of hydrogen bromide being obtained.

The following hydrochlorides were prepared by the action of dry hydrogen chloride on the various ketones. They are all unstable in presence of water, with which they give the original ketones.

Benzylideneacetone hydrochloride, $C_{10}H_{10}O, HCl$, dense oil; the *dihydrochloride*, $C_{10}H_{10}O, 2HCl$, obtained by cooling with ice and salt, forms a dense, reddish-brown oil.

Salicylideneacetone hydrochloride, $C_{10}H_{10}O_2, HCl$, is a dark reddish-violet oil; the *dihydrochloride*, $C_{10}H_{10}O_2, 2HCl$, forms an orange-yellow powder.

Anisylideneacetone hydrochloride, $C_{11}H_{12}O_2, HCl$, is dark green, and the *dihydrochloride*, $C_{11}H_{12}O_2, 2HCl$, an orange-yellow powder.

Vanillylideneacetone hydrochloride, $C_{11}H_{12}O_3, HCl$, has a dark peacock-blue colour, and decomposes slowly in the air, giving the ketone.

Methylvanillylideneacetone hydrochloride, $C_{12}H_{14}O_3, HCl$, has a garnet-red colour.

Cinnamylideneacetone hydrochloride, $C_{12}H_{12}O, HCl$, forms a semi-fluid mass with metallic, yellow reflection.

Benzylidenepiperonylideneacetone hydrochloride, $C_{18}H_{14}O_3, 2HCl$, resembles colcothar in appearance.

Benzylideneinnamylideneacetone hydrochloride, $C_{19}H_{16}O, 2HCl$, is a peacock-blue compound, and the free ketone dissolves in concentrated sulphuric acid, giving a cochineal-red solution.

Anisylidenecinnamylideneacetone dissolves in concentrated sulphuric acid, giving an intense peacock-blue coloration, and forms two hydrochlorides: the *dihydrochloride*, $C_{20}H_{18}O_2, 2HCl$, which is a green powder with metallic lustre, and the *trihydrochloride*, $C_{20}H_{18}O_2, 3HCl$, which is dark grey.

Piperonylideneinnamylideneacetone forms a dark violet solution in sulphuric acid, and yields the *hydrochloride*, $C_{20}H_{16}O_3, 2HCl$, m. p. 97° (decomp.), which is a green powder with metallic lustre.

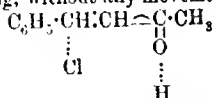
The following general conclusions are drawn from the results obtained by the authors and by Vorländer and Mumme (*loc. cit.*).

With ketones of the types $\text{CHR}:\text{CH}\cdot\text{CO}\cdot\text{R}$, $\text{CHR}:\text{CH}\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{R}$,
 $\text{CHR}:\text{CH}\cdot\text{CO}\cdot\text{CH}:\text{CHR}$, $\text{CHR}:\text{CH}\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{CH}:\text{CHR}$,
 $\text{CHR}:\text{CH}\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{CH}:\text{CH}\cdot\text{CH}:\text{CHR}$,

where R represents a substituted aryl or alkyl residue, the number of mols. of hydrogen chloride added at the ordinary temperature is, in general, the same as the number of double linkings in the $\alpha\beta$ -position. But the reaction is influenced by the substituent groups of the ketone molecule.

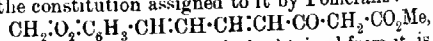
If, in dibenzylideneacetone, which unites readily and in definite molecular proportions with hydrogen chloride, the two hydrogen atoms combined with the carbon atom adjacent to the carbonyl group are replaced by methyl groups, no definite addition of hydrogen chloride occurs either at the ordinary temperature or at 0° . The introduction of methoxyl groups into the ketone molecule also favours the combination with hydrogen chloride. The substituent groups also influence the colour of the hydrochlorides, which, with colourless ketones, are yellow; with yellow ketones containing one double linking and of the type of benzylideneacetone, red, and with ketones containing two or three double linkings, green.

The formation of two series of compounds, one stable and colourless and the other unstable and coloured, by the action of halogen hydracids on unsaturated aromatic ketones cannot be explained either by a difference in the positions assumed by the atoms in the molecule or by a different spacial arrangement of the atoms. The colourless, stable derivatives behave like additive halogen compounds, and are formed according to Thiele's law (Abstr., 1899, i, 554), the application of which to ketones of the types under consideration shows that, if the addition of the hydracid is effected successively, it can only result in the formation of derivatives with one mol. of the acid for ketones with only one double linking and of derivatives with two mols. of acid in the case of ketones with two double linkings. The unstable, coloured additive derivatives are formed by the engaging of the partial valencies due to the double linking, without any movement of the latter, thus:

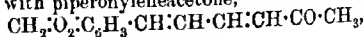


These compounds hence represent the first phase of the reaction of
 addition of the halogen hydracids. T. H. P.

Kawa Root [of *Piper methysticum*]. E. WINZHEIMER (*Arch. Pharm.*, 1908, 246, 338—365).—Besides confirming and extending the results of Pomeranz, the author has mainly investigated the constitution of yanguonin. The root contains: resins, 5.3% (of which 23% acids, 77% esters); methysticin, 0.30%; ψ -methysticin, 0.268%; yanguonin, 0.184%; an alkaloid, 0.022%; two glucosides, 0.69%; an amorphous acid, insoluble in water, 0.7—0.8%, and sugar. Methysticin has the constitution assigned to it by Pomeranz:

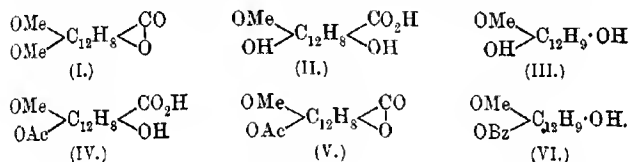


or a very similar one, since methysticol, obtained from it, is now proved to be identical with piperonyleneacetone,

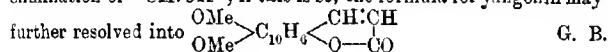


previously synthesised by Scholtz. The *phenylhydrazone* of methysticol melts at 152—152.5°; the *p-bromophenylhydrazone* at 162—163°; the *semicarbazone* at 199—199.5°; *benzylidenemethysticol*, $C_{20}H_{16}O_3$, at 110—111°; its *phenylhydrazone* at 187.5—188°, and *piperonylidene-methysticol* at 195—195.5°. ψ -Methysticin is, like methysticin, an ester of methystic acid; pale yellow leaflets, m. p. 113—114°; the analytical results are doubtful.

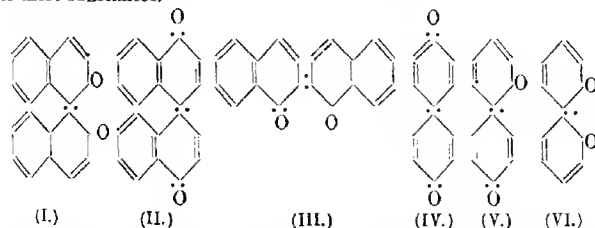
Yanگونin (I) has the composition $C_{15}H_{14}O_4$ (and not $C_{17}H_{12}O_5$, or $C_{10}H_8O_3$, as previously supposed). It contains two methoxyl groups, and appears to be a lactone; potassium hydroxide transforms it into *yangonic acid* (II), needles, m. p. 126—126.5°. At its melting point, or in boiling alcohol, this acid loses carbon dioxide, being converted into *yangonol* (III), yellow leaflets, m. p. 92—92.5°. When yangonic acid is heated with acetic anhydride, *acetylyangonic acid* (IV), m. p. 230°, and *acetylyangonic lactone* (V), m. p. 131—132°, are formed.



Yanگونol forms a *monobenzoyl* derivative (VI), yellow plates, m. p. 103°. On fusion with potassium hydroxide, yangonin yields a small quantity of a crystalline *acid*, m. p. 210—211°, free from methoxyl and probably having the composition $C_{11}H_{10}O_5$. It is regarded as being derived from yangonic acid (like benzoic from cinnamic acid) by the elimination of $-\text{CH}:\text{CH}-$; if this is so, the formula for yangonin may be



Binuclear Quinones as Chromogens. HERMAN DECKER (*Annalen*, 1908, 362, 320—324).—Of the six formulae below, only I, III, and VI can form indigoid dyes according to Friedländer's view of these substances.



Nevertheless, two strongly coloured derivatives of (II) have now been obtained (see following abstract), and the strong dye, cedrret, is a derivative of (IV). The author proposes therefore to group all such substances under the name of "binuclear quinonoid dyes." The

meaning of the term quinonoid must be widened to include substances in which a group, $-S-$, $-O-$, $-NH-$, or $-CH_2-$, is substituted for $-C:C-$, as also those in which the quinonoid

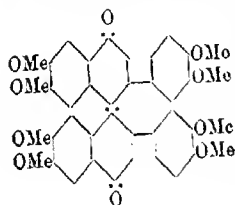
oxygen atom is displaced by a bivalent imine or hydrocarbon group. The binuclear quinonoid dyes fall then into place between the quinonoid and the triphenylmethane dyes. In this new group, the dye and leuco-compounds form two reciprocal systems of conjugated double linkings.

G. Y.

Formation of Naphthol Derivatives from Papaverine and the Binuclear Quinones of the Naphthalene Series. HERMAN DECKER (*Annalen*, 1908, 362, 305—319).—Decker and Dunaň's suggestion that the phenolic compound,

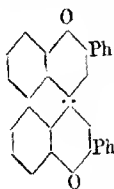
m. p. 180°, formed by the action of alkalis on papaverinium methylhaloids, has the annexed constitution (this vol., i, 204) is now confirmed, and the mechanism of the reaction by which it is formed is discussed.

6:7-Dimethoxy-2-*mp*-dimethoxyphenyl- α -naphthol gives a light green coloration with sulphuric acid, becoming violet when heated, forms crystalline alkali salts, and couples with α -diazonaphthalenes, forming insoluble, brownish-red azo-dyes. The pentamethoxy-compound,



$C_{10}H_4(OMe)_5 \cdot C_6H_3(OMe)_3$, formed by the action of methyl sulphate and alkali on the naphthol, crystallises in white leaflets, m. p. 162—163°, and sublimes unchanged. The blue dye, formed together with tetramethoxyphenylnaphthol by the action of alkalis on papaverinium methyl haloids in presence of air, or by the action of air on the impure naphthol containing veratraldehyde, but not on the pure

naphthol or by the action of oxidising agents on the naphthol in alkaline or acid solution, is considered to have the annexed constitution. It is obtained as a dark blue, glistening mass resembling indigotin, m. p. 225—235°, gives a green coloration with concentrated sulphuric acid, is decolorised by hot concentrated or alcoholic potassium hydroxide, and again forms the naphthol when treated with reducing agents.



When boiled with alcoholic potassium hydroxide in an atmosphere of hydrogen in a reflux apparatus, 1-phenylisoquinolinium methiodide evolves methylamine and yields 2-phenyl- α -naphthol, which is obtained as a resinous mass, gives the phenol reaction with diazo solutions, forms a methyl and a crystalline acetyl derivative, and on oxidation yields a violet dye, m. p. about 220°, annexed constitution. This forms a bluish-red solution in alcohol, or a violet-red in benzene or chloroform.

G. Y.

The Replacement of a Sulphonic Group by Hydroxyl in Anthraquinone- α -sulphonic Acid and its Derivatives. FARBEN-FABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 197649).—It has been found that by heating anthraquinone- α -sulphonic acid and its more highly sulphonated derivatives with aqueous sodium carbonate at 190–200°, the sulphonyl groups in α -positions are replaced by hydroxyl. Anthraquinone-1:5- and -1:8-disulphonic acids yield respectively anthrarufin and chrysazin, with small quantities of 1-hydroxyanthraquinone-5- and -8-sulphonic acids as intermediate products. Anthraquinone- α -sulphonic acid itself furnishes erythrohydroxyanthraquinone. G. T. M.

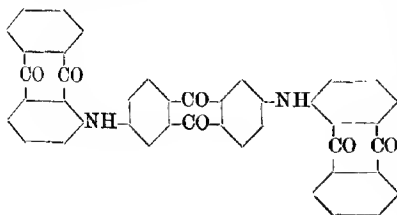
Preparation of Hydroxyanthrarufin and Hydroxychrysazin. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 196980).—, 1:2:5-Trihydroxyanthraquinone is readily obtained by heating anthrarufin with a mixture of sodium and potassium hydroxides in the presence of water and sodium nitrate. The employment of the mixture of alkali hydroxides gives a much better result, the oxidation to the trihydroxy-derivative being complete and without production of 1:2:5:6-tetrahydroxyanthraquinone. G. T. M.

Preparation of 1:5- and 1:8-Hydroxyanthraquinonesulphonic Acids. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 197607).—When heated with a mixture of calcium hydroxide and water at 140–150°, 1:5- and -1:8-anthraquinonedisulphonic acids are readily converted into 1-hydroxyanthraquinone-5- and -8-sulphonic acids, which are obtained in the form of their sodium salts. G. T. M.

Preparation of Hydroxyanthrarufin and Hydroxychrysazin. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 195028).—1:2:5-Trihydroxyanthraquinone (*hydroxyanthrarufin*), m. p. 273–274°, triacetyl derivative, m. p. 228°, was obtained by fusing anthrarufin with sodium nitrate and aqueous sodium hydroxide at 180–185°. 1:2:8-Trihydroxyanthraquinone (*hydroxychrysazin*), orange needles, m. p. 230°, triacetyl derivative, m. p. 219°, was obtained under similar conditions from chrysazin. G. T. M.

Preparation of Complex Dianthraquinonyldiaminoanthraquinones. BADISCHE ANILIN UND SODA-FABRIK (D.R.-P. 197554. Compare this vol., i, 456).—Complex anthracene colouring matters suitable for vat-dyeing are produced by condensing the amino- and diamino-anthraquinones with $\beta\beta$ -dihalogenated anthraquinones containing the two halogen atoms in different rings.

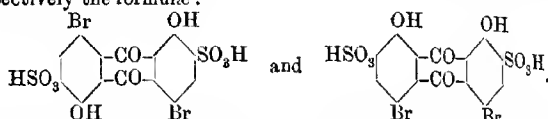
Di-1'-anthraquinonyl-2:6-diaminoanthraquinone is obtained by condensing 2:6-dichloro-anthraquinone and 1-aminoanthraquinone with anhydrous sodium acetate and cuprous chloride in boiling nitrobenzene. Similar compounds are produced from 2:7-dibromoanthraquinone and 1-aminoanthraquinone,



and 2:6-dichloroanthraquinone and 1:5-diaminoanthraquinone; they dissolve in concentrated sulphuric acid to green solutions, and furnish yellow or brownish-red leuco-derivatives in the hyposulphite vat.

G. T. M.

Preparation of *p*-Dibromoanthrarufin- and Dibromochrysazindisulphonic Acids. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 197082).—The sodium hydrogen salts of anthrarufindisulphonic and chrysazindisulphonic acids when treated with bromine in aqueous solution furnish the corresponding salt of dibromoanthrarufindisulphonic and dibromochrysazindisulphonic acids, which have respectively the formulæ:



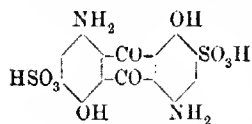
These products are yellow, crystalline salts moderately soluble in water.

G. T. M.

Preparation of Phenanthroanthraquinone. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 194328).—*Phenanthroanthraquinone*, yellow needles, m. p. 234°, is obtained by heating equal parts of pheanthrylbenzoyl-*o*-carboxylic acid and phosphoric oxide at 150° until the product is no longer soluble in aqueous alkalis. The crude quinone is dissolved in the form of its dihydro-derivative by alkaline hyposulphite and re-precipitated from this solution by aerial oxidation.

G. T. M.

Preparation of Diaminoanthrarufindisulphonic Acid. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 195139).—



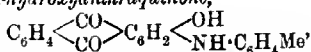
Diaminoanthrarufindisulphonic acid, blue needles, is readily obtained by stirring together sodium *p*-dibromoanthrarufindisulphonate, aqueous ammonia (20%), and a small amount of copper powder at 30–40°. Other halogenated anthra-

quinonesulphonic acids behave in a similar manner.

G. T. M.

Condensation of Quinizarin with Aromatic Amines. EUGÈNE GRANMOUGIN (*Chem. Zentr.*, 1908, i, 2178–2179; from *Rev. Gén. Mat. color*, 1908, 12, 37–39).—Quinizarin is readily reduced to *leucoquinizarin* by moistening it with alcohol, dissolving in very dilute sodium hydroxide solution, and treating with sodium hydrogen sulphite at the boiling temperature. It crystallises in yellow to orange needles, m. p. 155°.

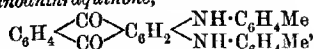
1: *o*-Toluidino-4-hydroxyanthraquinone,



is prepared by heating leucoquinizarin with *o*-toluidine and acetic

acid to 120—125°; dark violet crystals, m. p. 166°. The *acetate* is a violet-black, crystalline substance, m. p. 149°.

1:4-*Di-o-toluidinoanthraquinone*,



is obtained by heating leucoquinizarin with *o*-toluidine, acetic acid, and anhydrous boric acid; it crystallises in small, dark brown needles, m. p. 223°. The *di-m-toluidine* derivative of quinizarin, prepared in a similar manner, crystallises in small, dark blue needles, m. p. 183°, and the *di-diethyl-p-phenylenediamine* derivative, $\text{C}_{34}\text{H}_{36}\text{O}_2\text{N}_4$, nearly black needles, m. p. 234—235°. The *mono-p-toluidine* derivative is violet-black, m. p. 183°; *di-p-toluidine* derivative, m. p. 218°.

J. V. E.

Preparation of Alkyl Camphorates. J. D. RIEDEL (D.R.-P. 196152. Compare this vol., i, 352).—Inactive camphoric acid, like its dextrorotatory constituent, reacts in alkaline solution either with methyl sulphate or the alkyl arylsulphonates to furnish its normal esters. *Methyl dl-camphorate*, colourless oil, D 1.073/22°, and b. p. 145—147°/20 mm., is thus obtained by adding alternately potassium hydroxide and methyl sulphate to an aqueous solution of potassium *dl* camphorate.

G. T. M.

Preparation of *iso*Bornyl Esters of the Fatty Acids from Pinene Hydrochloride or Hydrobromide. CHEMISCHE FABRIK VON HEYDEN AKT.-GES. (D.R.-P. 196017. Compare this vol., i, 351).—*iso*Bornyl esters of the fatty acids are produced by heating together pinene hydrochloride or hydrobromide, the requisite mineral acid, and a zinc salt of some acid, other than a halide or an oxidising agent. Thus *isobornyl formate* is derived from pinene hydrochloride, formic acid, and anhydrous zinc sulphate. *isobornyl acetate* is produced by the interaction of pinene hydrochloride, acetic acid, and zinc *p*-toluenesulphonate.

G. T. M.

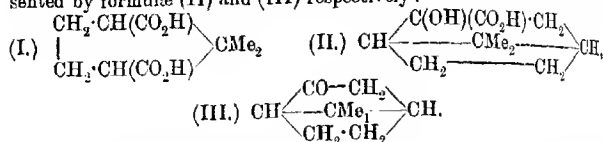
Preparation of the *iso*Bornyl Esters of Fatty Acids from Pinene Hydrochloride or Hydrobromide. CHEMISCHE FABRIK VON HEYDEN AKT.-GES. (D.R.-P. 194767. Compare this vol., i, 351).—Although zinc chloride and other metallic salts, such as cobalt or cuprous chloride, when heated separately with pinene hydrochloride and glacial acetic acid, give rise only to small yields of *isobornyl acetate*, yet when a mixture of the zinc salt and that of another heavy metal is employed, a good yield of the required ester is obtained.

Thus good yields of *isobornyl acetate* are obtained by boiling a mixture of pinene hydrochloride, glacial acetic acid, and zinc chloride with cuprous, cupric, ferrous, aluminium, cadmium, cobalt, or nickel chloride. *isobornyl formate* results in a similar manner from pinene hydrochloride, formic acid, manganous chloride, and zinc chloride.

G. T. M.

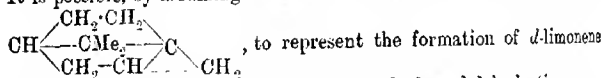
Terpenes and Ethereal Oils. XCIV. The Fenchone Series. OTTO WALLACH [with PAUL VIVCK] (*Annalen*, 1908, 362, 174—200. Compare Wallach, this vol., i, 429; Abstr., 1898, i, 486; 1899, i, 65; 1901, i, 331; 1907, i, 541).—The oxidation of *dl*-fenchene by an

aqueous alkaline solution of potassium permanganate has been re-investigated, and the results obtained previously (Abstr., 1899, i, 65) confirmed. The hydrocarbon is exceedingly stable towards this oxidising agent, yielding *dl*-hydroxyfenchenic acid, m. p. 154°, and *apocamphoric* acid. *dl*-Hydroxyfenchenic acid is oxidised by lead peroxide and sulphuric acid to fenchocamphorone, which latter is converted by alkaline potassium permanganate into *apocamphoric* acid. Assuming *apocamphoric* acid to have the generally accepted formula (I), then *dl*-hydroxyfenchenic acid and fenchocamphorone must be represented by formulæ (II) and (III) respectively:



The conclusion might also be drawn that *dl*-fenchene has the structural formula $\begin{array}{c} \text{CH}_2 \cdot \text{CH} - \text{C} : \text{CH}_2 \\ | \\ \text{CMe}_2 \\ | \\ \text{CH}_2 \cdot \text{CH} - \text{CH}_2 \end{array}$, but the great stability of the hydrocarbon towards permanganate is not in agreement with this formula.

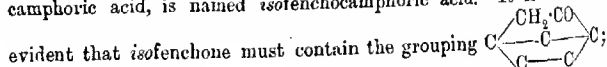
The *dl*-fenchene used in this investigation was obtained by adding sodium nitrite and acetic acid to an aqueous solution of fenchylamine hydrochloride. An oil, b. p. 175—178°, was obtained together with the fenchene, and was found on investigation to be a mixture of *d*-limonene, cineole, and dipentene; the latter substance was probably formed as a secondary product from either the *d*-limonene or cineole. It is possible, by assuming *dl*-fenchene to have the structural formula



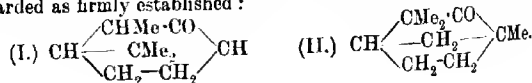
and cineole by alternate processes of hydrolysis and dehydration.

The "*isofenchene*" obtained by Bertram and Helle (Abstr., 1900, i, 398) from *isofenchyl* alcohol is shown to be identical with *dl*-fenchene obtained from fenchyl alcohol (compare Wallach, Abstr., 1899, i, 65).

isoFenchone, derived from *isofenchyl* alcohol, is oxidised by permanganate to an acid, $\text{C}_{10}\text{H}_{16}\text{O}_4$, which, since it is isomeric with camphoric acid, is named *isofenchocamphoric* acid. It is therefore



further, since fenchone and *isofenchone* behave so differently on oxidation, they must have widely different constitutions. Neither the author's fenchone formula (I) nor Semmler's formula (II) is to be regarded as firmly established:



dl-Fenchene, prepared from fenchylamine, is the purest as yet obtained; it has b. p. 156–157°, D_{10}^4 0.869, n_D^{19} 1.4724, and n_D^{18} – 32.2° (in 1-dm. tube). The *dibromide*, $C_{10}H_{16}Br_2$, prepared by acting on the hydrocarbon with bromine in acetic acid, forms colourless crystals, m. p. 87–88°, $[\alpha]_D^{25} + 42.83^\circ$ (in ethyl acetate).

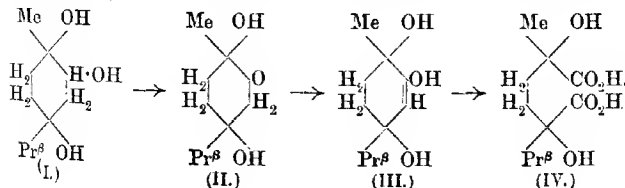
dl-Hydroxyfenchenic acid is now found to have m. p. 154°, $[\alpha]_D^{25} - 62.98^\circ$ (in ether).

*iso*Fenchone readily forms a *semicarbazone*, $C_{11}H_{19}ON_3$, which crystallises in needles, m. p. 221–222°, $[\alpha]_D^{25} - 8.27^\circ$ (in methyl alcohol). *Bromoiso*fenchone, $C_{10}H_{15}OBr$, is readily formed by the action of bromine on *isofenchone* at the ordinary temperature; it forms colourless crystals, m. p. 56–57°, $[\alpha]_D^{25} - 164.1^\circ$ (in ethyl alcohol).

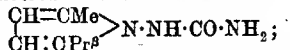
*iso*Fenchocamphoric acid, $C_{10}H_{16}O_4$, obtained by oxidising *isofenchone* or *isofenchyl* alcohol with an aqueous alkaline solution of potassium permanganate, has m. p. 158–159°, $[\alpha]_D^{25} - 12.75^\circ$ (in ether); the *silver* salt, $C_{10}H_{14}O_4Ag_2$, was prepared and analysed.

The following derivatives of *l*-fenchone were prepared; they melt at the same temperatures as the corresponding *d*-fenchone derivatives; the values in brackets are the m. p.'s of the racemic compounds: *isofenchyl phenylcarbamate*, m. p. 107° (94°); *isofenchone semicarbazone*, m. p. 221–222° (223–224°); *isofenchoneoxime*, m. p. 82° (133°); *bromoiso*fenchone, m. p. 56–57° (46–47°); *isofenchocamphoric acid*, m. p. 158–159° (174–175°).
W. H. G.

Terpenes and Ethereal Oils. XCV. Alcohols of the Terpinene Series (Terpinenols). OTTO WALLACH (*Annalen*, 1908, 362, 261–284. Compare this vol., i, 429).—I. *Degradation Products of Terpinene-4-ol* (Δ^1 -*Menthene-4-ol*). [With FRITZ MEISTER.]—It was shown previously (*Abstr.*, 1907, i, 943) that, on oxidation with alkaline permanganate, trihydroxyterpane yields an optically active acid, m. p. 205–206°, and an optically inactive isomeric acid, m. p. 188–189°. It is found now that, when heated with permanganate and dilute sulphuric acid at 60–70°, both acids yield dimethyl-acetonylacetone, and must therefore have the constitution (IV). The oxidation of the trihydroxyterpane (I) is considered to lead in the first place to the formation of a dihydroxyketone (II), which changes in the alkaline solution into the enolic form (III), and then undergoes further oxidation with resolution of the ring between the carbon atoms 2 and 3. Such a reaction may take place also in other cases, and may explain the difference in the oxidation products sometimes obtained on resolution of cyclic compounds with permanganate and with chromic acid:

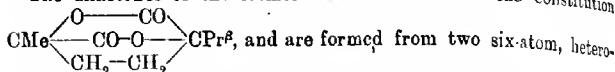


The semicarbazone of dimethylacetonylacetone (Posner, *Abstr.*, 1902, i, 82) is considered to have the constitution



it does not yield the ketone when heated with 10% sulphuric acid, is resinified by boiling with strong acids, and when heated alone evolves vapours giving the pyrrole reaction.

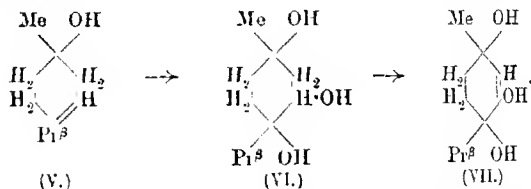
The dilactones of the isomeric acids must have the constitution



cyclic nuclei (compare Le Sueur, *Trans.*, 1907, 93, 716).

II. *Synthesis of $\alpha\alpha'$ -Dihydroxy- α -methyl- α' -isopropyladipic Acid.* [With FRITZ MEISTER.]—With the object of confirming the constitution ascribed to the isomeric acids obtained by oxidation of trihydroxyterpane, dimethylacetonylacetone was treated with potassium cyanide and hydrochloric acid at 0° , and subsequently on the water-bath; on distillation with steam, the product yielded the dilactone, m. p. $72-73^\circ$, which on hydrolysis with boiling alkali was converted into the optically inactive acid, m. p. $188-189^\circ$.

III. *Terpinene-1-ol [Δ^3 -p-Menthene-1-ol] and its Degradation Products.* [With FRITZ MEISTER.]—The unsaturated alcohol, $\text{C}_{10}\text{H}_{17}\cdot\text{OH}$, b. p. $208-210^\circ$, obtained from the fractions of commercial terpineol boiling at low temperatures cannot be, as was thought (*loc. cit.*), identical with terpinene-4-ol, as the trihydroxyterpane, m. p. 120° , obtained from it yields when heated with acids, not carvenone, but a ketone with an odour of menthone. The alcohol is now considered to be terpinene-1-ol (V). This, on oxidation, must yield 1:3:4-trihydroxyterpane (VI), which, on further oxidation, should be converted by way of the enolic form (VII) into $\alpha\alpha'$ -dihydroxy- α -methyl- α' -isopropyladipic acid (IV). The identity of the acid thus obtained has been confirmed by its conversion into the dilactone, m. p. 72° , and into dimethylacetonylacetone.



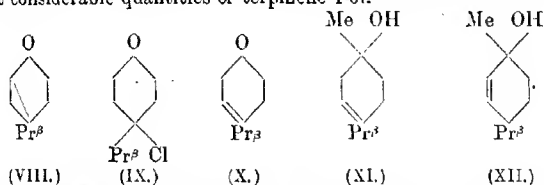
The ketone (Δ^1 -menthene), $\text{CMe} \begin{array}{c} \text{CH}=\text{CO} \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \text{CHPr}^{\beta}$, formed from 1:3:4-trihydroxyterpane, has b. p. $235-237^\circ$, $D_{20}^{20} 0.9375$, $n_D^{20} 1.4875$, and forms a sparingly soluble semicarbazone, m. p. $224-226^\circ$, which yields the ketone again when heated with sulphuric acid. When treated with sodium in ethereal solution, the ketone yields a pinacone and an alcohol, which is oxidised by chromic acid, forming *menthone*. The semicarbazone of this has m. p. $210-212^\circ$. A comparison of the physical properties of Δ^1 -menthene with those of carvenone,

carotacetone, Δ^4 -menthenone, and Callenbach's menthenone (see Rabe and Rahm, Abstr., 1904, i, 757; Merling, Abstr., 1905, i, 349), shows that the new ketone most closely resembles carvenone.

Δ^4 -Menthenone, purified by conversion into its oxime and liberation by means of sulphuric acid, has b. p. 213° , D^{21}_D 0.918, n^{21}_D 1.4720; the semicarbazone has m. p. 142° ; the dibromide, $C_{10}H_{16}OBr_2$, m. p. 36° . On reduction, menthenone yields a mixture of stereoisomeric menthols, including *i*-menthol, which forms a semicarbazone, m. p. 212° .

IV. *Synthesis of the Two Tertiary Alcohols of the Terpinene Series, Terpinene-4-ol (Δ^1 -Menthene-4-ol) and Terpinene-1-ol (Δ^3 -Menthene-1-ol).*—The formation of terpinene-4-ol from sabinene hydrate was described previously (this vol., i, 430). The crystalline sabinene hydrate, formed by the action of magnesium methyl iodide on sabina ketone, has $[\alpha]_D +53.67^\circ$, and when shaken with sulphuric acid yields terpinene-4-ol, which has $[\alpha]_D +10.53^\circ$, and is identical with the terpienol from cardamom and majorana oils, but may contain small amounts of the inactive alcohol.

[With RICHARD HEYER.]—Terpinene-1-ol (XI) is prepared from abinaketone (VIII) by conversion of this by way of its hydrochloride IX into Δ^3 -isopropylhexenone (X) and treatment of the product with magnesium methyl iodide. Δ^3 -isoPropylhexenone has b. p. $15-96^\circ/12$ mm., D^{22}_D 0.944, n^{22}_D 1.4817. Terpinene-1-ol has b. p. $12-97^\circ/14$ mm., D^{24}_D 0.9210, n^{24}_D 1.4778, and loses water when distilled under the ordinary pressure, forming phellandrene. The ethylene linking undergoes transmigration during the decomposition of the terpienol, or Δ^3 -isopropylhexenone isomerises to Δ^2 -isopropylhexenone during the Grignard reaction, in which case the resulting alcohol must be phellandrene hydrate (XII). As on oxidation the synthetic alcohol yields 1:3:4-trihydroxyterpane, it must contain at least considerable quantities of terpiene-1-ol.



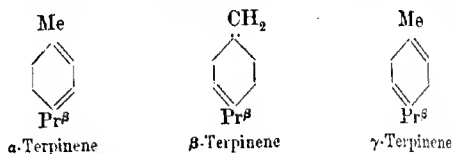
V. *Other Syntheses in the Terpinene Group.*—The action of magnesium isopropyl iodide on sabina ketone leads to the formation of a tertiary alcohol, which is obtained as a viscid oil, b. p. $102-107^\circ/14$ mm., and, when shaken with dilute sulphuric acid, slowly forms the *terpin*, $OH \cdot CPr^3 \cdot \begin{matrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{matrix} \cdot CPr^3 \cdot OH$. This crystallises in plates, m. p. 139° , and reacts readily with hydrogen haloids in glacial acetic acid solution. The dichloride, $C_{12}H_{22}Cl_2$, has m. p. $111-112^\circ$; the dibromide, m. p. $120-121^\circ$. G. Y.

Terpenes and Ethereal Oils. XCVI. Terpinene and its Modifications. OTTO WALLACH (*Annalen*, 1908, 362, 285-304).—

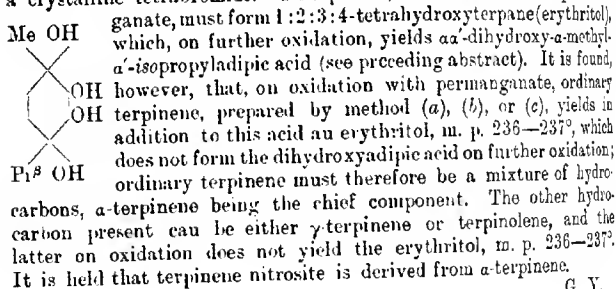
1. β -Terpinene.— β -Terpinene (Abstr., 1907, i, 1058) is now found

to have b. p. 173—174°, D^{20}_D 0.838—0.840, n^{20}_D 1.4751—1.4754. With bromine in alcoholic-etheral solution, it forms a sparingly soluble tetrabromide, $C_{10}H_{16}Br_4$, crystallising in prisms, m. p. 154—155°, and when treated with water and oxygen in presence of sunlight is converted into dihydrocuminolaldehyde, which is further oxidised to cuminaldehyde. Oxidation of β -terpinene with permanganate in aqueous solution leads to the formation of a neutral product, which distils at 225°/10 mm., yielding small amounts of a crystalline substance, and when treated with dilute sulphuric acid, without previous distillation, yields an oil having a strong odour of cuminaldehyde and forming a semicarbazone, m. p. 201—202°.

II. *Constitution of Ordinary Terpinene*.—It has been shown previously (Abstr., 1907, i, 943) that terpinene must be one of, or a mixture of two or three of, the three substances having the annexed formulæ. These three substances yield the same dihydrohaloids.



Terpinene has now been obtained (a) from the dihydrochloride, m. p. 52°, (b) by inversion of pinene, and (c) synthetically from sabinone. Ordinary terpinene, b. p. 179—181°, cannot contain β -terpinene, as this has now been found to boil at a lower temperature than limonene, to form terpinene nitrosite only slowly and incompletely, and to yield oxidation products; moreover, ordinary terpinene does not form a crystalline tetrabromide. α -Terpinene, on oxidation with permanganate, must form 1:2:3:4-tetrahydroxyterpane (erythritol), which, on further oxidation, yields $\alpha\alpha'$ -dihydroxy- α -methyl- α' -isopropyladipic acid (see preceding abstract). It is found, however, that, on oxidation with permanganate, ordinary terpinene, prepared by method (a), (b), or (c), yields in addition to this acid an erythritol, m. p. 236—237°, which does not form the dihydroxyadipic acid on further oxidation; ordinary terpinene must therefore be a mixture of hydrocarbons, α -terpinene being the chief component. The other hydrocarbon present can be either γ -terpinene or terpinolene, and the latter on oxidation does not yield the erythritol, m. p. 236—237°. It is held that terpinene nitrosite is derived from α -terpinene.



Philippine Terpenes and Essential Oils. I. RAYMOND F. BACON (*Philippine J. Sci.*, 1908, 3, 49—64).—When a mixture of limonene hydrochloride and ether is treated with magnesium and the product decomposed with cold dilute sulphuric acid, a hydrocarbon, $C_{10}H_{16}$, b. p. 174—176°, is produced, which has D^{20}_D 0.8257, n^{20}_D 1.4585, and $[\alpha]^{20}_D$ 90.3°, and is probably identical with the dihydrolimonene obtained by Semmler (Abstr., 1903, i, 505) by the

reduction of limonene hydrochloride with sodium and alcohol. The hydrochloride of this compound was prepared and submitted to the Grignard reaction, when a hydrocarbon, $C_{10}H_{16}$, b. p. 171—174°, was obtained, which has D_4^{20} 0.8052, n_D^{20} 1.4459, and $[\alpha]_D^{20}$ 3.7°. When benzaldehyde is added to the product of the action of magnesium on limonene hydrochloride, the hydrocarbon, $C_{10}H_{16}$, is liberated, and a compound, $C_{10}H_{15} \cdot COMgCl$, is produced, which is decomposed by dilute acids with formation of benzaldehyde, and is converted by heat into benzoin and other substances. Acetone reacts with the magnesium compound in a similar way.

When magnesium benzyl chlorid is treated with benzaldehyde, phenylbenzylcarbinol, m. p. 67—68°, is produced. E. G.

Philippine Terpenes and Essential Oils. II. Ylang-ylang Oil. RAYMOND F. BACON (*Philippine J. Sci.*, 1908, 3, 65—86).—Determinations have been made of the sp. gr., rotatory power, refractive index, and ester number of samples of Philippine ylang-ylang oil of different grades and origin. The ester number of first-grade oils is usually about 100, whilst that of second-grade oils rarely exceeds 80. The refractive index of the former is rarely more than 1.4900, whereas that of the latter approaches 1.5000. This difference is due to the fact that the second-grade oils contain more sesquiterpenes and resins. For the same reason, $[\alpha]_D$ of the first-grade oils is usually below -45° , whilst that of the second-grade is -60° or more.

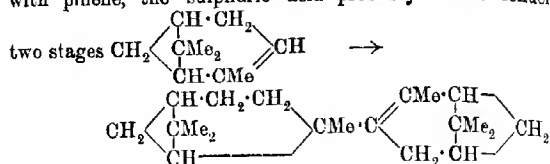
A study of the composition of the oil has confirmed, on the whole, the work of previous observers, and has shown that the following substances are present: esters of formic, acetic, valeric (1), benzoic, and salicylic acids; methyl and benzyl alcohols; pinone, cadinene, and other terpenes and sesquiterpenes; linalool, geraniol, and safrole; eugenol, isoeugenol, and *p*-cresol, probably as methyl ethers; and creosol.

The following esters have been prepared for comparison: *benzyl salicylate*, b. p. 186—188°/10 mm.; *benzyl benzoate*, b. p. 315—320°; *benzyl methyl ether*, b. p. 166—168°; *benzyl formate*, b. p. 84—85°/10 mm.; *geranyl methyl ether*, b. p. 100—105°/10 mm. and 208—212°/760 mm.; *linalyl methyl ether*, b. p. 189—192°, and *geranyl benzoate*, b. p. 198—200°/15 mm. E. G.

Method of Obtaining Resins from Turpentine and the Preparation from them of Lacs, Varnishes, &c. E. I. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 800—805).—This method consists in treating turpentine oil with sulphuric acid of 66° B. and formaldehyde, neutralising with ammonia, separating the ammonium sulphate, and heating with ammonia. After drying at 70—80°, a yellowish-brown resin is obtained, which is soluble in alcohol, benzene, toluene, ether, or acetic acid, giving yellow solutions. It also dissolves in solvent naphtha or ethyl acetate, and the solutions in these solvents form quick-drying, elastic lacs.

The chemical constituents of the lacs obtained were not determined, but it is probable that they consist of a hydrocarbon, or mixture of

hydrocarbons, produced by a series of condensations. For example, with pinene, the sulphuric acid probably causes condensation in



Continuation of this process would lead to still more complicated hydrocarbons. The formaldehyde probably reacts with the mobile hydrogen atoms, giving $\cdot\text{CH}_2\cdot\text{OH}$ groups. The alcohols so formed would lose water on heating, giving rise to methylene derivatives of terpenes and polyterpenes.

T. H. P.

Resins from Conifers, and Treatment of the Resinous Sap from *Pinus maritima*, *P. sylvestris*, and other Species. W. SCHKATELOFF (*Chem. Zentr.*, 1908, i, 2097—2100; from *Moniteur scient.*, 1908, [4], 22, 217—227. Compare *Abstr.*, 1907, i, 213).—From studying the composition of the resin from *Pinus sylvestris*, the author comes to the conclusion that in all ordinary resins, such as colophony, galipot, resinous saps, &c., the same resin acid is present in the following isomeric modifications: (1) α -sylvic acid, a white, crystalline powder, m. p. 143—144°, $[\alpha]_D - 73.67^\circ$; (2) β -sylvic acid, crystallising in three-sided plates, m. p. 160°, $[\alpha]_D - 92.5^\circ$; (3) γ -sylvic acid, crystallising in long needles or three-sided plates, m. p. 179—180°, optically inactive. Of these modifications, β -sylvic acid appears to be identical with the abietic acid described by Mach and Levy, and γ -sylvic acid identical with pyromaric acid described by Laurents. A yellow, acid, uncrystallisable resin, called by Unverdorben pinic acid, was found accompanying these three isomeric acids in all crude products. It is produced from the isomeric resin acids by oxidation when exposed to the air. The evidence so far obtained indicates that the formula of the resin acids may be $\text{C}_{20}\text{H}_{28}\text{O}_2\cdot\text{H}_2\text{O}$, an unsaturated compound containing two double linkings. Considerable contradiction and confusion as to the properties of these resin acids is caused by the difficulty of investigating them. As an instance of this, it is stated that if α -sylvic acid from *P. sylvestris* is melted, a pale colophony is obtained, $[\alpha]_D - 73.5^\circ$; the same acid from *P. abies excelsa* gives a colophony, $[\alpha]_D - 74.1^\circ$; which, if heated in an air-oven to 170°, shows $[\alpha]_D - 60^\circ$, and $[\alpha]_D - 18^\circ$ after heating to 180—180°, finally becoming inactive.

The Properties of Resinous Saps from Various Pines.—(a) From *Pinus sylvestris*: gives, when steam-distilled, 15—16% turpentine oil, $[\alpha]_D + 22^\circ$ to $+24^\circ$, or rectified over sodium hydroxide, $[\alpha]_D + 25.1^\circ$, $D^{20}_D 0.867$. The acid present in the sap is α -sylvic acid. (b) From *P. abies excelsa*: gives very little resin; the resin sap contains about 13.4% oil, $D^{20}_D 0.873$, $[\alpha]_D - 13.2^\circ$, and also α -sylvic acid, m. p. 143° and $[\alpha]_D - 74.1^\circ$. (c) *Larix sibirica* gives very little resin sap, 14.13% oil of $D^{20}_D 0.870$, $[\alpha]_D - 14.3^\circ$, and β -sylvic acid. (d) *Pinus cembra* gives only 6% oil of $D^{20}_D 0.865$, $[\alpha]_D + 14.04^\circ$; another portion

contained 20% oil of b. p. 155—156° and $[\alpha]_D + 17^\circ$, and from the solid resin, β -sylvic acid was obtained. (e) *P. taurica* gave a quantity of the same resin as *P. maritima*; the resinous sap contained 20% oil of D^{10} 0.861 and $[\alpha]_D - 75.9^\circ$, and the solid resin, α -sylvic acid. (f) *Abies sibirica*: the resin sap is a very aromatic, clear liquid containing 28% oil, D^{10} 0.8751, $[\alpha]_D - 35.6^\circ$, but no crystallisable substance. (g) *Pinus strobus*: the resin sap is similar to that of ordinary pine, and contains α -sylvic acid.

J. V. E.

Decomposition of Amygdalin by Emulsin. LEOPOLD ROSENTHALER (*Arch. Pharm.*, 1908, 246, 365—366).—Feist (this vol., i, 437) regards *d*-benzaldehydecyanohydrin, formed when emulsin acts on amygdalin, as a primary product in the hydrolysis. The author, however, has now shown experimentally that *d*-benzaldehydecyanohydrin is formed from benzaldehyde and hydrocyanic acid by emulsin, and is therefore a secondary synthetic product.

G. B.

Constitution of Vicianin. I. GABRIEL BERTRAND and GUSTAVE WEISWILLER (*Compt. rend.*, 1908, 147, 252—254).—Vicianin (Abstr., 1907, i, 68), like amygdalin and Dakin's isoamygdalin (*Trans.*, 1904, 85, 1512), when dissolved in concentrated sulphuric acid gives a curmin-red coloration, slowly whilst cold, rapidly on heating. Schiff (Abstr., 1900, i, 49) considered this reaction as characteristic of mandelonitrile. The presence of the group $\cdot O \cdot CHPh \cdot CN$ in vicianin is proved by two reactions: (1) When an aqueous solution of the crystallised glucoside is treated at 35° with an extract of the seeds of *Vicia angustifolia*, hydrogen cyanide (estimated by Denigès' method, Abstr., 1896, ii, 385) and benzaldehyde (estimated by conversion into the phenylhydrazone) are produced in equal molecular quantities. (2) By evaporating to dryness vicianin (4 grams) with fuming hydrochloric acid (25 c.c.), *l*-mandelic acid is produced. The acid obtained has m. p. 132—133° (on Maquenne block) and $[\alpha]_D - 153.3^\circ$ (at 18° and 1% solution), whilst Walden (Abstr., 1896, ii, 137) found m. p. 131—132° and $[\alpha]_D - 133.06^\circ$. The conclusion is drawn that vicianin, like amygdalin, is a derivative of *l*-mandelonitrile.

E. H.

Action of Hydrochloric Acid on Santonin and its Derivatives. Mechanism of the Formation of Desmotroposantonin. LUIGI FRANCESCONI and G. CUSMANO (*Gazzetta*, 1908, 38, ii, 101—110).—It has been stated by Wedekind (*Chem. Zeit.*, 1902, No. 13), and by Wedekind and Schmidt (*Arch. Pharm.*, 1906, 44, 623), that santonin acid is transformed into desmotroposantonin by the action of hydrochloric acid. The authors show that no such change takes place, and that the method of preparation of santonin acid probably employed by Wedekind (Abstr., 1898, i, 596) gives mixtures of santonin acid with santoninic acid or santonin, which mixtures have, in some cases, a melting point practically the same as that given by Wedekind, and cannot be freed from impurity by crystallisation from a mixture of alcohol and ether.

Santonin acid and desmotroposantonin are not acted on by dry hydrogen chloride. When cooled with a mixture of ice and salt,

santonin absorbs 2 mols. of hydrogen chloride, one of which is eliminated rapidly at the ordinary temperature in an atmosphere of hydrogen chloride, and the other, slowly in presence of an extraneous gas. Both these hydrochlorides yield santonin when treated with water or sodium hydroxide, and are related to santonin in the same way as the coloured, unstable additive products of ketones with the halogen hydracids are related to the ketones themselves (compare this vol., i, 801). Both these hydrochlorides change gradually into a monohydrochloride, which is not capable of absorbing hydrogen chloride, and yields desmotroposantonin by the action of water or by spontaneous elimination of hydrogen chloride. The formation of those different hydrochlorides and that of desmotroposantonin from them are explained in the same way as the formation of the various hydrochlorides of the unsaturated, aromatic ketones (*loc. cit.*).

T. H. P.

Sapotoxin and Sapogenin from *Agrostemma githago*. II. J. BRANDL (*Arch. exp. Path. Pharm.*, 1908, 59, 245—268).—A second sapotoxin can be obtained from the lead acetate precipitate from the crude sapotoxin, which can be purified by precipitation by ethyl alcohol from the solution in methyl alcohol. It is designated *agrostemmic acid*. It has a considerably higher molecular weight than the *A*-sapotoxin. It yields on hydrolysis sapogenin, $C_{35}H_{54}O_{10}$, in a yield of 38%, and sugars, calculated as dextrose, in a yield of 50.67%. The sugars obtained by the hydrolysis of the saponins consist of dextrose and galactose, with possibly some arabinose.

The potassium salt of sapogenin methyl ester, when pure, has a composition corresponding with $C_{36}H_{55}O_{10}K$. By treating the potassium salt or its methyl esters with methyl sulphate, a series of methyl derivatives can be obtained, the yield of which varies with the conditions of experiment. The monomethyl derivative, which is crystalline, but has no definite m. p., corresponds with the formula $C_{36}H_{56}O_{10}$. The higher methyl derivatives are not crystalline.

By heating sapogenin with potassium hydroxide at 160—175°, an acid, $C_{30}H_{40}O_4$, is obtained, which does not melt at 290°, and yields a dimethyl ester, m. p. 231—232°. This acid is also obtained from dogs' faeces after ingestion of sapotoxin.

The toxic effects of the seeds of *Agrostemma githago*, of agrostemmic acid, and of the sapotoxin are similar. The seeds in quantities of 10 grams per kilo. in pigeons, and 15 grams per kilo. in hens, ingested *per os* cause death in two to three days. Vomiting, diarrhoea, salivary flow, and paralysis are the chief symptoms.

S. B. S.

Sweet Substances from *Eupatorium Rebaudianum* and Liquorice. PAUL RASENACK (*Chem. Zentr.*, 1908, ii, 78—79; from *Arb. Kais. Gesundh.-Amt.*, 1908, 23, 420—443).—The sweet material which is contained chiefly in the leaves of *Eupatorium Rebaudianum* was obtained by extracting with alcohol and then precipitating with ether. The crude product separates from methyl alcohol in slender, white needles, which shrink at 180—190°, m. p. 200—210° (decomp.). The

composition of this substance appears to be $C_{42}H_{72}O_{31}$, and its behaviour towards salt solutions differs from that of glycyrrhizin.

When boiled with dilute sulphuric acid, it gives dextrose and a tasteless substance, forming small, prismatic crystals, m. p. 226—227°, which are sparingly soluble in water, and appear to have the composition $C_{30}H_{40}O_5$. The author has investigated the sweet material from liquorice root, and detected the presence of saccharose therein. From the results of analysis, the formula for glycyrrhizic acid is considered to be $C_{44}H_{60}O_{18}$.

J. V. E.

Aminolactones from Diacetone Alcohol. MORITZ KOHN (*Monatsh.*, 1908, 29, 509—518. Compare this vol., i, 829).—The use of diacetone alcohol (β -methylpentane- β -ol- δ -one) instead of diacetone-amine in the Bucherer and Zelinsky reaction (*loc. cit.*) leads in a similar manner to the formation of tetrahydrofuran derivatives in place of those of pyrrolidone.

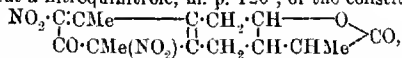
4-Amino-5-keto-2:2:4-trimethyltetrahydrofuran, $O \begin{matrix} \diagup CO-CH_2-NH_2 \\ \diagdown CMe_2-CH_2 \end{matrix}$, m. p. 30—34°, b. p. 122—124°/14—16 mm., yields a phenylthiocarbamide, m. p. 195—198°. 4-Methylamino-5-keto-2:2:4-trimethyltetrahydrofuran, $C_8H_{15}O_2N$, b. p. 108—111°/12 mm., forms a phenylthiocarbamide, m. p. 152—154°.

The reaction between the alcohol, potassium cyanide, and dimethylamine hydrochloride leads to the ultimate formation of a liquid, b. p. 113°/12 mm., which is a mixture of Franke and Kohn's 4-hydroxy-5-keto-2:2:4-trimethyltetrahydrofuran (*Abstr.*, 1907, i, 816) and 4-dimethylamino-5-keto-2:2:4-trimethyltetrahydrofuran, $C_8H_{17}O_2N$, of which the platinumchloride, and the methiodide with its aurichloride and platinumchloride are mentioned.

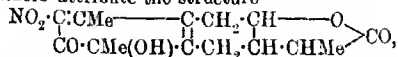
C. S.

Action of Nitric Acid on Desmotroposantonin. GUIDO BARGELLINI and V. DA CONTO (*Gazzetta*, 1908, 38, ii, 41—52. Compare *Abstr.*, 1907, i, 931).—When oxidised by means of chromic acid, desmotroposantonin yields a compound which, with phenylhydrazine in dilute acetic acid, gives an insoluble, red product, but the amount obtained was too small to admit of its further study.

On treating desmotroposantonin with nitric acid under the conditions given by Andreocci (*Abstr.*, 1898, i, 266), the authors find that the first compound formed is not the nitrodesmotroposantonin described by Andreocci, but a nitroquinol, m. p. 120°, of the constitution



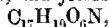
which decomposes readily into one or other of the three compounds described by Andreocci (*loc. cit.*), according to the conditions. To the compound, m. p. 240°, obtained by Andreocci by the action of hot dilute nitric acid or cold concentrated nitric acid on desmotroposantonin, the authors attribute the structure



which is more in accord with its mode of formation from the nitroquinol and with its behaviour as a nitroquinol than is the con-

stitution suggested by Andreocci. The authors could not obtain Andreocci's third substance, m. p. 145°, in a pure state.

The *nitroquinitrole*, $C_{15}H_{16}O_7N_2$, obtained as an amorphous, white powder, m. p. about 120° (decomp.), like all quinitroles, decomposes readily with evolution of oxides of nitrogen. When decomposed by means of methyl or ethyl alcohol, it gives an almost quantitative yield of nitrodesmotroposantonin, $C_{15}H_{17}O_5N$, which separates from alcohol in trimetric crystals [A. ROSATI: $a:b:c=0.4133:1:2.2646$], m. p. 189–190°, $[\alpha]_D^{25} + 115.38^\circ$. Nitrodesmotroposantonin exhibits all the characters of the nitrophenols, and yields an *acetyl* derivative,



which crystallises from alcohol in white needles, m. p. 166–167°, $[\alpha]_D^{25} + 111.79^\circ$.

The nitroquinol, m. p. 237–240° (decomp.), which can also be obtained by heating the nitroquinitrole or nitrodesmotroposantonin on the water-bath with nitric acid (D 1.23), dissolves readily in concentrated sulphuric acid, giving a cherry-red solution, and yields an *acetyl* derivative, $C_{17}H_{19}O_6N$, m. p. 186–188°. When reduced by means of sulphuric acid, the nitroquinol is converted into nitrodesmotroposantonin, whilst reduction by zinc and acetic acid yields a red, amorphous substance, which appears to be analogous to that obtained by Wedekind (Abstr., 1905, i, 134) by reducing benzene azodesmotroposantonin with stannous chloride and hydrochloric acid.

[With A. MANNINO.]—*l*-Desmotroposantonin behaves towards nitric acid in the same way as desmotroposantonin, a nitroquinitrole being first formed. The *nitroquinol*, $C_{15}H_{17}O_5N$, crystallises from acetic acid in colourless needles, m. p. 218–220° (decomp.), dissolves in concentrated sulphuric acid, giving a red coloration, and is levorotatory.

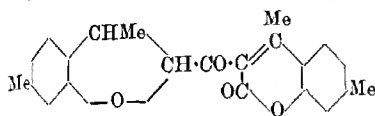
T. H. P.

Conversion of Coumarins into Coumarinic Acids and *o*-Coumaric Acids. KARL FRIES and W. KLOSTERMANN (*Annalen*, 1908, 362, 1–29).—It has been shown previously (Abstr., 1906, i, 273) that 7-methylcoumarin, 4:7-dimethylcoumarin, and 3:4:7-trimethylcoumarin differ in their behaviour towards aqueous alkalis. The rate of formation of coumarinic acids from these substituted coumarins, and also from 4:7-dimethyl-3-ethylcoumarin and 3-benzyl-4:7-dimethylcoumarin, on treatment with an aqueous solution of potassium hydroxide has now been measured. It is found that the velocity with which the coumarin is converted into the corresponding coumarinic acid decreases, not only with an increase in the number, but also in the size, of the alkyl or aryl group. This is shown by the following comparative values representing the velocity of formation of the coumarinic acid: 7-methylcoumarin = 150, 4:7-dimethylcoumarin = 100, 3:4:7-trimethylcoumarin = 75, 4:7-dimethyl-3-ethylcoumarin = 45, 3-benzyl-4:7-dimethylcoumarin = 35.

The behaviour of these substituted coumarins on treatment with sodium ethoxide is far more complicated. Ebert has shown (Abstr., 1885, 391) that coumarin and 7-methylcoumarin are converted into the corresponding *o*-coumaric acids when heated with sodium ethoxide. It has now been found possible to isolate the hitherto unknown ethyl

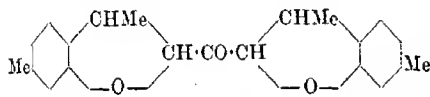
esters of these acids, formed as intermediate products during the reaction. The esters themselves are colourless, but their alkali salts are yellow; it is therefore not improbable that the salts have the quinonoid structure $O:C_6H_4:CH:CH:C(OEt)ONa$. This view receives support from the fact that an alcoholic ammoniacal solution of the ester reduces silver nitrate, whereas neither *o*-coumaric acid nor ethyl cinnamate reduces silver nitrate under similar conditions. The yellow, aqueous solutions of these salts are not fluorescent.

4:7-Dimethylcoumarin when heated with sodium ethoxido or



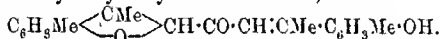
methoxide is not converted into the corresponding coumaric acid, but yields a ketone which probably has the annexed formula. It is

proposed to name the group $C_6H_4 \begin{smallmatrix} CH_2 \\ \diagup \quad \diagdown \\ O \end{smallmatrix} CH \cdot CO-$, hydrocoumarilyl, hence this ketone is 3-[2:5-dimethylhydrocoumarilyl]-4:7-dimethylcoumarin. It is converted by aqueous alkalis into another ketone, thus: $C_{22}H_{20}O_4 + H_2O \rightarrow C_{21}H_{22}O_3 + CO_2$. This new compound is



probably 1-[2:5-dimethylhydrocoumarilyl]-2:5-dimethyl hydrocoumarone, having the annexed formula.

The solubility of this substance in alkalis and the formation of a methoxy-derivative on treating a solution in alcoholic sodium ethoxido with methyl iodide may be explained by assuming a transformation into an enolic form, but the compound does not give a coloration with ferric chloride and does not react with copper acetate. It is possible that in the formation of the salts, the hydrocoumarone ring opens, forming an *o*-hydroxybenzylidene derivative,



This would account for the yellow colour of the salts, but the fact that the methoxy-derivative is colourless then becomes remarkable.

4:6-Dimethylcoumarin, like the isomeric 4:7-dimethyl compound, is converted by sodium ethoxido into a ketone, $C_{21}H_{22}O_3$, similar to that just described.

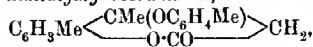
3:4:7-Trimethylcoumarin, 4:7-dimethyl-3-ethylcoumarin, and 3-benzyl-4:7-dimethylcoumarin are converted by sodium ethoxido into sodium salts of the corresponding coumarinic acids.

The effect of the presence of alkyl groups on the reconversion of coumaric acids into coumarins is very marked; thus β :4-dimethyl-*o*-coumaric acid and β :5-dimethyl-*o*-coumaric acid in acetic acid are converted by concentrated hydrochloric acid at the ordinary temperature into the corresponding coumarins in a few hours, whilst, under the same conditions, *o*-coumaric acid and 4-methyl-*o*-coumaric acid remain practically unchanged even during several days. The tendency of β -alkyl-*o*-coumaric acids to change into coumarins is shown

by the fact that the latter compounds slowly separate from solutions of the acids in aqueous sodium carbonate.

Ethyl o-coumarate, $C_{11}H_{12}O_3$, crystallises in small, compact plates, m. p. 87° ; the *sodium salt* crystallises in yellow leaflets. *Ethyl 4-methyl-o-coumarate*, $C_{13}H_{14}O_3$, crystallises in plates, m. p. 105° .

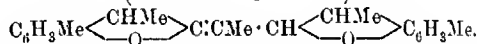
4-Tolyl-oxy-4 : 7-dimethylhydrocoumarin,



is formed together with 4 : 7-dimethylcoumarin if in the preparation of the latter from *m*-cresol and ethyl acetoacetate the quantity of the sulphuric acid employed is less than that previously given (Abstr., 1906, i, 276). It crystallises in long, glistening prisms, m. p. 220° , and is converted by strong acids into *m*-cresol and 4 : 7-dimethylcoumarin.

3-[2 : 5-Dimethylhydrocoumarinyl]-4 : 7-dimethylcoumarin, $C_{23}H_{24}O_3$, crystallises in slender, white needles, m. p. 257° (decomp.). 1-[2 : 5-Dimethylhydrocoumarinyl]-2 : 5-dimethylhydrocoumarone, $C_{21}H_{22}O_3$, crystallises in monoclinic prisms, m. p. 185.5° . The molten substance sets to a glassy mass, m. p. $93-95^\circ$; the liquefied substance again becomes solid at about 140° , and then has m. p. 185.5° . The *hydrobromide*, $C_{21}H_{22}O_3 \cdot HBr$, forms yellow crystals; the *oxime*, $C_{21}H_{23}O_3N$, crystallises in small plates, m. p. 220° ; the *phenylhydrazone*, $C_{27}H_{28}O_3N_2$, forms slender, pale yellow needles, m. p. 198° . The ketone, $C_{21}H_{22}O_3$, when treated with magnesium methyl iodide and then with dilute sulphuric acid, is converted into a *substance*,

having the formula $C(C_6H_3Me \begin{array}{c} \text{CHMe} \\ \text{O} \end{array} \text{CH})_2 \cdot CH_2$ or



It forms large crystals, m. p. 145° . The ketone, $C_{21}H_{22}O_3$, yields a *methoxy-derivative*, $C_{22}H_{24}O_3$, crystallising in long, flat plates, m. p. 165° , and an *ethoxy-derivative*, $C_{23}H_{26}O_3$, crystallising in prisms, m. p. 156° .

4 : 6-Dimethylcoumarin is converted by a hot aqueous solution of potassium hydroxide into β : 5-dimethyl-o-coumaric acid, $C_{11}H_{12}O_3$; it crystallises in small leaflets, decomposing with evolution of carbon dioxide at about 138° .

A *ketone*, $C_{21}H_{22}O_3$, is formed by the action of sodium ethoxide on 4 : 6-dimethylcoumarin. It is very similar in properties to the isomeric ketone derived from the 4 : 7-compound, forming compact, colourless crystals, m. p. 199° ; the *oxime*, $C_{21}H_{23}O_3N$, crystallises in microscopic needles, m. p. 120° .

4 : 7-Dimethyl-3-ethylcoumarin, $C_{13}H_{14}O_2$, prepared by the action of concentrated sulphuric acid on a mixture of ethyl ethylacetoacetate and *m*-cresol, crystallises in long, spear-shaped needles, m. p. 87° .

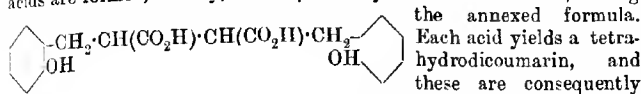
3-Benzyl 4 : 7-dimethylcoumarin, $C_{18}H_{18}O_2$, prepared from ethyl benzylacetoacetate and *m*-cresol, crystallises in long, white needles, m. p. 117° .

W. H. G.

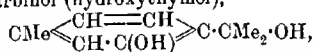
Reduction of Coumarins with Zinc Dust in Alkaline Solution. KARL FRIES and G. FICKEWIRTH (*Annalen*, 1908, 362, 30-48).—With the object of finding a simple method of preparing

hydrocoumarins from coumarins, reduction by means of zinc dust in alkaline solution was tried, but without success. The results obtained show, however, that derivatives of coumarin containing an alkyl group in the pyrone ring are quite different in their chemical behaviour from coumarin itself.

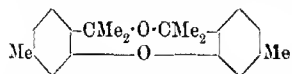
Coumarin is converted by zinc dust in alkaline solution chiefly into mellilotic acid, but at the same time two isomeric tetrahydrodicoumaric acids are formed, namely, α - and β -tetrahydrodicoumaric acids, having



α - and β -tetrahydrocoumarins, $C_6H_4 \begin{array}{c} \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \\ \text{O} \quad \text{CO} \quad \text{CO} \quad \text{O} \end{array} C_6H_4$ (compare Dyson, *Trans.*, 1887, 51, 61). When 4:7-dimethylcoumarin is treated in the same way as coumarin, it yields 2-hydroxy-4-methylphenyldimethylcarbinol (hydroxythymol),



2-hydroxy- β :4-dimethylstyrene, and thymol; the quantity of each substance formed depends on the duration of the action, the first compound formed being hydroxythymol. The part played by the zinc dust in the formation of the latter substance is not yet clear, for, although the formation of this alcohol is not due to simple reduction, yet the reaction proceeds in a different direction when the zinc dust is not present. It is probable that at first the 4:7-dimethylcoumarin is converted into β :4-dimethyl- α -coumaric acid, which by the addition of water changes into β :2-hydroxy-4-methylphenyl- β -methylhydracrylic acid, $OH \cdot C_6H_3Me \cdot CMe(OH) \cdot CH_2 \cdot CO_2H$; the latter substance then loses carbon dioxide, yielding hydroxythymol. Since hydroxythymol, when heated, readily loses water, yielding 2-hydroxy- β :4-dimethylstyrene or its polymeride (compare this vol., i, 160), it is evidently a tertiary alcohol having the formula given above. Although hydrochloric acid and hydrobromic acid convert hydroxythymol into the polymerised form of 2-hydroxy- α :4-dimethylstyrene, hydriodic acid acts on it, forming a substance identical with the condensation product obtained by Gaebel (*Diss.*, Marburg, 1903) from *m*-cresol and acetone, to which



the annexed formula was assigned.
The normal reduction product of 4:7-dimethylcoumarin, namely, β :4-dimethylhydrocoumaric acid, is obtained by using sodium amalgam as the reducing agent. This acid is very unstable, and readily changes into 4:7-dimethylhydrocoumarin.

4:6-Dimethylcoumarin is converted by zinc dust and alkali into 2-hydroxy-5-methylphenyldimethylcarbinol and 6-hydroxy- α :3-dimethylstyrene (compare this vol., i, 160). The compound corresponding with thymol, namely, 2-hydroxy-5-methylcoumeu, seems to be formed only with difficulty, and has not yet been obtained pure.

3:4:7-Trimethylcoumarin remains practically unattacked by zinc dust in alkaline solution.

α -Tetrahydrodicoumaric acid, $C_{18}H_{18}O_6$, crystallises in plates, m. p.

280—282°. When heated alone for some time at 280°, or in acetic acid, it is converted into *α-tetrahydrodicoumarin*, $C_{18}H_{14}O_4$, crystallising in glistening needles, m. p. 284°.

β-Tetrahydrodicoumaric acid, $C_{18}H_{18}O_6$, forms compact prisms, m. p. 158°.

β-Tetrahydrodicoumarin, $C_{18}H_{14}O_4$, crystallises in glistening, slender needles, m. p. 256°.

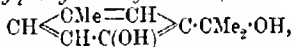
2-Hydroxy-4-methylphenyldimethylcarbinol (hydroxythymol),



forms small, glistening, spear-shaped crystals, m. p. 64°. It is converted by hydriodic acid into a substance, $C_{20}H_{24}O_2$, crystallising in colourless, compact prisms, m. p. 132°. A substance, $(C_{10}H_{13}O)_n$, crystallising in small leaflets, m. p. 186°, is formed, together with hydroxythymol, by the action of zinc dust on 4:7-dimethylcoumarin in alkaline solution; mol.-wt. determinations by the boiling-point method point to *n* being 2.

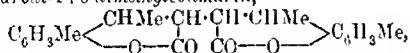
β:4-Dimethyl-α-hydrocoumaric acid, $C_{11}H_{14}O_3$, crystallises in hook-like needles, m. p. 98°; it loses water when heated, yielding 4:7-dimethylhydrocoumarin, obtained as an oil. If, during the reduction of 4:7-dimethylcoumarin with sodium amalgam, the liquid is kept slightly acid by means of acetic acid, a small quantity of a substance, m. p. 250°, is obtained. It is probably a tetramethyltetrahydrodicoumarin.

2-Hydroxy-5-methylphenyldimethylcarbinol,



prepared from 4:6-dimethylcoumarin, crystallises in rosettes of small, glistening prisms, m. p. 82°.

α-Tetrahydrodi-4:6-dimethylcoumarin,

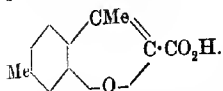


produced by the action of zinc dust on 4:6-dimethylcoumarin in alkaline solution, forms small needles, m. p. 284°. The *β-isomeride* is best prepared from *β:5*-dimethylcoumaric acid; it forms small, colourless crystals, m. p. 254°. W. H. G.

Coumarone and Hydrocoumarone Derivatives from 4:7-Dimethylcoumarin. KARL FRIES and G. FICKEWIRTH (*Annalen*, 1908, 362, 49—53).—The object of this investigation was the preparation of 2:5-dimethylhydrocoumarone, the latter being required for purposes of identification. This substance was first prepared by von Baeyer and Seuffert (*Abstr.*, 1901, i, 216) by a method which gives but a poor yield. It was therefore obtained by reducing 2:5-dimethylcoumarilic acid to 2:5-dimethylhydrocoumarilic acid, which, when distilled with soda-lime, yields 2:5-dimethylhydrocoumarone.

4:7-Dimethylcoumarin is converted by bromine in chloroform into 3-bromo-4:7-dimethylcoumarin, $C_{11}H_9O_2Br$; it crystallises in long, white, silky needles, m. p. 138°, and is converted by a boiling alcoholic

solution of potassium hydroxide into 2:5-dimethylcoumarilic acid.



The latter substance forms small, compact crystals or oblique-angled plates, m. p. about 213° (decomp.); the *ethyl* ester crystallises in small, slender needles, m. p. 38°. The acid, when distilled with soda-

lime, yields 2:5-dimethylcoumarone, b. p. 218° (compare Stoemer, Abstr., 1900, i, 650).

2:5-Dimethylhydrocoumarilic acid, $C_{11}H_{12}O_3$, is obtained by reducing 2:5-dimethylcoumarilic acid with sodium amalgam. It forms small crystals, m. p. 95°, and, when distilled with soda lime, yields 2:5-dimethylhydrocoumarone, $C_{10}H_{12}O$, an oil, b. p. 222°.

W. H. G.

Preparation of Double Salts from Caffeine and Alkali Metaphosphates. F. HOFFMANN-LA ROCHE & CIE (D.R.-P. 194533).—Caffeine and the alkali metals form soluble, stable dimetaphosphates.

Caffeine sodium dimetaphosphate, $C_8H_{10}O_2N_4 \cdot NaHP_2O_6$, is prepared by adding caffeine to an aqueous solution of sodium hydrogen dimetaphosphate and evaporating to dryness under reduced pressure.

G. T. M.

The Alkaloids of Chinese Corydalis Tubers. K. MAKOSHI (*Arch. Pharm.*, 1908, 246, 381—400).—After much labour, corydaline, corybulbine, protopine, dehydrocorydaline (not hitherto known to occur naturally), and two new alkaloids were isolated. The first new alkaloid, $C_{20}H_{17}O_4N$, is an isomeride of berberine, and a quaternary base; the *hydrochloride*, $C_{20}H_{15}O_4NCl \cdot 2H_2O$, forms red needles, resembling sanguinarine hydrochloride, but is not precipitated by ammonia; *aurichloride*, $C_{20}H_{15}O_4NCl \cdot AuCl_3$, reddish-brown needles, decomposing above 280° without melting. By zinc and hydrochloric acid, this alkaloid is reduced to a substance, $C_{20}H_{21}O_4N$, colourless needles, m. p. 218—219°, not identical with hydroberberine.

The second new alkaloid, greyish-white needles, m. p. 197—199°, was only obtained in minute quantity, and is not identical with bulbocapnine, since it gives different colour reactions.

G. B.

Does Crystallisable Cocaine Occur in Java Coca? ANNE W. K. DE JONG (*Chem. Weekblad*, 1908, 5, 666—668).—Samples of the alkaloid obtained from both the old and young leaves of Java coca contain cocaine, the percentage being higher in that derived from the former source.

A. J. W.

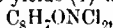
Oxidation by means of Picric Acid. Indulines from Aniline. A. BACOVESCU (*Chem. Zentr.*, 1908, i, 2034—2035; from *Buletinul d. Chimie*, 1908, 10, 3—5).—When aniline is successively heated with picric acid to about 225° and the mass purified from chloroform and ether, two substances, probably indulines, are obtained.

The reaction also takes place in the presence of hydrogen chloride. One substance is greyish-black, the other brown, and both dissolve in concentrated sulphuric or acetic acid, giving a blue solution.

J. V. E.

Preparation of Halogenated Anilides. A. MANNINO and L. DI DONATO (*Gazzetta*, 1908, 38, ii, 20—31).—The authors have applied the method used by Verda (*Abstr.*, 1903, i, 21) to the preparation of halogenated derivatives of various acetanilides. The latter were treated with mixtures of nitric acid (D 1.398) and hydrochloric (D 1.19) or hydrobromic acid (D 1.48) in various proportions. As a rule, these acid mixtures effect only a chlorinating or brominating action, but in some cases, for example, aceto-*o*-naphthalide, a nitro-group is introduced into the molecule. It is remarkable that, in these reactions, hydrolysis of the acetyl group never occurs, although this takes place easily when the acetanilides are heated with hydrochloric acid alone. The products obtained are individual compounds in a pure state, and the yields are almost quantitative.

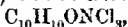
With acetanilide and nitric and hydrochloric acids, 2:4-dichloroacetanilide is obtained if the action is restricted, and 2:4:6-trichloroacetanilide if the action is prolonged. With nitric and hydrobromic acids, 2:4-dibromoacetanilide is formed. With *o*-chloroacetanilide, the product is 2:4:6-trichloroacetanilide or 2-chloro-4-bromoacetanilide. *m*-Chloroacetanilide yields (1) a *dichloroacetanilide*,



crystallising from alcohol in white needles, m. p. 187—188°, and probably not identical with 3:5-dichloroacetanilide, also melting at 187°, since under the above conditions the halogen generally enters in the *o*- or *p*-position to the NHAc group; (2) 3-chloro-2-bromoacetanilide (1), $\text{C}_8\text{H}_6\text{ONClBr}$, which crystallises from 60% acetic acid in needles, m. p. 105—107°. *p*-Chloroacetanilide yields 2:4:6-trichloroacetanilide or 4-chloro-2-bromoacetanilide. *m*-Bromoacetanilide gives 4:6-dichloro-3-bromoacetanilide (1), $\text{C}_8\text{H}_3\text{ONCl}_3\text{Br}$, which crystallises from alcohol in tufts of flesh-coloured needles, m. p. 194—195°, or 2:4:5-tribromoacetanilide. With *m*-nitroacetanilide a chlorodinitroacetanilide (1), m. p. about 200°, is formed. *p*-Nitroacetanilide yields 2-chloro-4-nitroacetanilide or a yellow bromoderivative, m. p. about 115°, which was not obtained sufficiently pure to analyse.

Aceto-*o*-toluidide yields a dichloroaceto-*o*-toluidide, m. p. 155—156° (compare Verda, *loc. cit.*), or 5-bromo-2-acetotoluidide. Aceto-*p*-toluidide gives (1) 2:3:6- or 2:3:5-trichloroaceto-*p*-toluidide, $\text{C}_9\text{H}_7\text{ONCl}_3$, which separates from alcohol in crystals, m. p. 178—180°, and (2) 2:6-dibromoaceto-*p*-toluidide, $\text{C}_9\text{H}_7\text{ONBr}_2$.

Aceto-*m*-xylylidide gives (1) 3:5:6-trichloroaceto-*m*-xylylidide,



which crystallises from aqueous alcohol in white needles, m. p. 190—192°, and, when boiled with dilute hydrochloric acid, yields the corresponding trichloro-*m*-xylylidine, m. p. 203°, or (2) 3:5:6-tribromoaceto-*m*-xylylidide, $\text{C}_{10}\text{H}_8\text{ONBr}_3$, which separates from alcohol in crystals, m. p. 246—248°.

Aceto- α -naphthalide yields (1) the chloronitroaceto- α -naphthalide, m. p. 219°, which was prepared by Verda (*loc. cit.*), which, on boiling with dilute hydrochloric acid in alcoholic solution, gives a compound, $C_{10}H_7O_2N_2Cl$, crystallising from alcohol in yellow needles, m. p. about 230°, or (2) 3:8-dibromoaceto- α -naphthalide. Aceto- β -naphthalide gives (1) a red, oily chloro-derivative; (2) a tribromoaceto- β -naphthalide, m. p. 250° (decomp.), which gives, on hydrolysis, a compound, m. p. 125°; since 1:3:6-tribromo- β -naphthylamine has m. p. 143°, it is probable that the tribromoaceto- β -naphthalide is not the 1:3:6-compound which has been described as having the m. p. 250°.

T. H. P.

Resolution of Racemic Amines by means of Camphoramic Acids. MLLÉ. G. FREYRON (*Ann. Chim. Phys.*, 1908, [viii], 15, 140—144).—According to Wallach (*Abstr.*, 1906, i, 160), primary amines can be prepared by the addition of formic or acetic acid to a mixture of ammonium formate with an aldehyde or ketone. The author finds, however, that this method does not serve for the preparation of α -phenylethylamine, which can be obtained in a yield equal to 50% of the ketone employed by heating 10 grams of acetophenone with 20 grams of pure, dry ammonium formate to 180—190° for six hours.

When condensed with camphoric anhydride, α -phenylethylamine yields a mixture of the two stereoisomeric camphoramic acids, $CO_2H \cdot C_3H_7 \cdot CO \cdot NH \cdot CHMePh$, which, by fractional crystallisation, can be separated into: (1) a dextro-fraction, $C_{13}H_{17}O_3N$, $[\alpha]_D^{20} + 64.92^\circ$, and (2) a laevo-fraction, $[\alpha]_D^{20} - 50.52^\circ$, both of which have m. p. 161—162°. When boiled with 30% hydrochloric acid, the *d*-compound yields the amine, b. p. 81°/15 mm., which gives a dextrorotatory hydrochloride, m. p. 159—160°, but was obtained in quantity too small to admit of analysis.

Thus, although the α -camphoramic acids are easily and rapidly prepared, they do not afford a good means for resolving racemic bases into their optically active components. With bases containing only aliphatic radicles, the resolution is more difficult than with aromatic compounds, so much so that in no case has more than one derivative exhibiting a constant m. p. and rotatory power been obtained (compare Locquin, *Abstr.*, 1907, i, 593).

T. H. P.

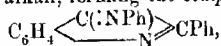
New Method of Preparing some Simple Ethers. II. TH. VAN HOVE (*Bull. Acad. roy. Belg.*, 1908, 540—551. Compare *Abstr.*, 1907, i, 173). The author has extended his investigation on the preparation of ethers by the action of quinoline hydrochloride on primary alcohols to secondary and tertiary alcohols, with the results that, whereas the secondary alcohol yields the corresponding ether and ethylene hydrocarbon, the tertiary alcohol yields ethylene hydrocarbons only. When isopropyl alcohol (1 mol.) is heated with quinoline hydrochloride (0.2 mol.) in sealed tubes at 160° for eight days, the products consist of isopropyl ether, isopropyl chloride, and propylene, together with an isopropylquinoline and diisopropylquinoline. The isopropyl ether, b. p. 68—68.2°, $D_4^{16.2}$ 0.7319 (*Zander, Abstr.*, 1882,

1259, gives D^{20}_D 0.7247), obtained amounted to 24.5% of the theoretical yield; the *isopropylquinoline*, b. p. 280—300°, yielded a *picrate*, m. p. 160—161°, and is therefore not identical with any of the *isopropylquinolines* already described (Widman, Abstr., 1886, 465; Döbner, Abstr., 1887, 504; Spady, Abstr., 1886, 263); *diisopropylquinoline*, b. p. 300—320°, forms a *picrate*, m. p. 226—228°.

When trimethylcarbinol is heated for three days at 160° with quinoline hydrochloride, the principal products consist of *isobutylene* and *diisobutylene*.
M. A. W.

Catalytic Action of Finely-divided Metals on Compounds containing Nitrogen. MAURICE PADOA and G. SCAGLIARINI (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 728—731).—Whereas 2-methylindole is obtained on passing quinoline vapour over reduced nickel heated at 260—280° (Abstr., 1906, i, 765), 3-methylindole is formed together with a little quinoline when tetrahydroquinoline is similarly treated. The action probably occurs owing to the intermediate formation of propylaniline by the breaking of bond 4—5, or of 2-methylamino-1-ethylbenzene by the breaking of bond 2—3, probably the latter, because propylaniline does not produce a methylindole when heated with nickel at 300°.
W. A. D.

Indoles. ANGELO ANGELI and EUGENIO MORELLI (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 697—702).—The view that 3-nitrosoindoles are true nitroso-derivatives, $C_6H_4 \begin{smallmatrix} \text{C(NO)} \\ \text{NH} \end{smallmatrix} \gg CR$, is improbable in view of the fact that either the silver or sodium salt gives with ethyl iodide only one ethyl derivative; that obtained from 3-nitroso-2-phenylindole is red, and has m. p. 45°. The structure of the nitroso-indoles is discussed at some length; they are probably best regarded as oximes, $C_6H_4 \begin{smallmatrix} \text{C(NO)} \\ \text{N} \end{smallmatrix} \gg CR$, derived from the tautomeric form, $C_6H_4 \begin{smallmatrix} \text{CH} \\ \text{N} \end{smallmatrix} \gg CR$, of the indoles. This view is confirmed by the fact that 2-phenylindole reacts with nitrosobenzene in alcoholic solution in presence of traces of alkali, forming the compound,



which crystallises from alcohol in crimson prisms, m. p. 155°. The action is compared with that of phenylacetonitrile and nitrosobenzene, $CH_2Ph \cdot CN + NO \cdot C_6H_5 = H_2O + NPh \cdot CPh \cdot CN$.

The compound, $C_6H_4 \begin{smallmatrix} \text{C(NPh)} \\ \text{N} \end{smallmatrix} \gg CMe$, prepared from 2-methylindole and nitrosobenzene, forms yellow crystals, m. p. 183°. The compound, $NMe_2 \cdot C_6H_4 \cdot N : C \begin{smallmatrix} \text{CMe} \\ \text{C}_6H_4 \end{smallmatrix} \gg N$, obtained similarly from 2-methylindole and nitrosodimethylaniline, forms red needles, m. p. 185°.
W. A. D.

Preparation of Anthranil. KALLE & Co. (D.R.-P. 194364. Compare Abstr., 1907, i, 908).—The dimercure derivative of *o*-nitro-

toluene forms a yellow chloride when mixed with 10% hydrochloric acid, and this product, when added to stronger hydrochloric acid (D 1.185), furnishes the hydrochloride of anthranil, from which this amide can be purified by distillation in steam.

G. T. M.

Aminopyrrolidone Derivatives from Mesityl Oxide and from Benzylideneacetone. MORITZ KOHN (*Monatsh.*, 1908, 29, 497—503).—Bucherer's and Zelinsky's modifications of Strecker's original method for the production of α -amino-acids have been applied by the author to β -amino-ketones, with the result that aminopyrrolidone derivatives are obtained instead of the expected α - γ -diamino-acids.

The interaction of aqueous methyl-diacyetonamino, powdered potassium cyanide (1 mol.), and concentrated aqueous ammonium chloride (1 mol.) at 5—10° leads, after hydrolysis of the diaminonitrile by concentrated hydrochloric acid, to the formation of 4-amino-5-

keto-1:2:2:4-tetramethylpyrrolidine, $\text{NMe} \begin{array}{c} \text{CO} - \text{CMe} \cdot \text{NH}_2 \\ | \\ \text{CMe}_2 \cdot \text{CH}_2 \end{array}$, b. p.

140—143°/17 mm., which is soluble in water, absorbs carbon dioxide, and forms a phenylthiocarbamide, m. p. 180—181°. By using methylamine hydrochloride in the place of ammonium chloride in the preceding reaction, 4-methylamino-5-keto-1:2:2:4-tetramethylpyrrolidine, $\text{C}_6\text{H}_5\text{ON}_2$, b. p. 128—130°/15—16 mm., is obtained, which also absorbs water or carbon dioxide, and yields a phenylthiocarbamide, m. p. 132—135°, and an acetyl derivative, m. p. 123—125.5°. 4-Dimethylamino-5-keto-1:2:2:4-tetramethylpyrrolidine, b. p. 130—140°/13 mm., obtained in a similar manner by using an aqueous-alcoholic solution of dimethylamine hydrochloride, forms a platinumchloride and a methiodide, from which the corresponding aurichloride and platinumchloride are obtained.

The constitution of the additive compound of benzylideneacetone and methylamine has been shown to be $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CHPh} \cdot \text{NHMe}$, since it can be converted by potassium cyanide and methylamine hydrochloride and subsequent hydrolysis into 4-methylamino-5-keto-

2-phenyl-1:4-dimethylpyrrolidine, $\text{NMe} \begin{array}{c} \text{CO} - \text{CMe} \cdot \text{NHMe} \\ | \\ \text{CHPh} \cdot \text{CH}_2 \end{array}$, h. p.

181°/13 mm., a colourless, odourless, viscous liquid, which is soluble in water, absorbs carbon dioxide, and forms a crystalline phenylthiocarbamide.

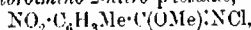
C. S.

Stereoisomeric Chloroimino-acid Esters. WILLIS STOSE HILPERT (*Amer. Chem. J.*, 1908, 40, 150—194).—Stieglitz and Earle (Abstr., 1904, i, 39) have shown that methyl chloroimino-*m*-nitrobenzoate exists in two stereoisomeric modifications, and Stieglitz and Hale have recently found (unpublished) that the corresponding ethyl ester exhibits the same phenomenon. The author now finds that methyl and ethyl chloroimino-*p*-nitrobenzoates, methyl chloroimino-2-nitro-*p*-toluate, and methyl and ethyl chloroimino- β -naphthoates also exist in stereoisomeric modifications, but no stereoisomerides are obtainable in the case of methyl chloroimino-*p*-bromo-*m*-nitrobenzoate

and methyl chloroimino-*p*-bromobenzoate. In the case of the first three pairs of stereoisomerides, the less stable form can be transformed into the more stable one by the action of chlorine, and the converse process also is possible to a small extent. In the case of the naphthalene derivatives, the change is brought about by boiling water. Further details are given for the separation of α - and β -methyl chloroimino-*m*-nitrobenzoates and for the transformation of one form into the other.

When *p*-nitrobenzonitrile is treated with methyl alcohol in benzene solution, it yields *methyl imino-p-nitrobenzoate*, a white, crystalline substance, m. p. 93—94°, which, with hypochlorous acid, gives *methyl chloroimino-p-nitrobenzoate*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{OMe})\text{NCl}$.

The crude substance is fractionally precipitated from its chloroform solution by light petroleum, whereby the α -(*syn*-)form is precipitated in needles, m. p. 99—100°, and the mother liquor yields the more stable β -(*anti*-)form in plates, m. p. 76°. *Ethyl chloroimino-p-nitrobenzoate*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{OEt})\text{NCl}$, is prepared similarly by the action of hypochlorous acid on the imino-ester obtained from *p*-nitrobenzonitrile and ethyl alcohol. By the same process of fractionation as used for the methyl ester, the α -(*syn*-)form was almost exclusively obtained in needles, m. p. 98—99°. The β -(*anti*-)form, which crystallised only to a very small extent along with the α -form, was isolated mechanically; it occurs in plates, m. p. 90°, and is the more unstable modification, being readily transformed into the α -form by chlorine. *n-Propyl chloroimino-p-nitrobenzoate*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{OPr}^n)\text{NCl}$, is an oil. *Methyl imino-2-nitro-p-toluate*, prepared from 2-nitro-*p*-tolunitrile and methyl alcohol, is a white, crystalline solid, m. p. 60—61°; the *hydrochloride* was analysed. On treatment with hypochlorous acid, the free ester yields *methyl chloroimino-2-nitro-p-toluate*,



which, when fractionally precipitated by light petroleum from its chloroform solution, yielded a mixture of the α -(*syn*-)form in plates, m. p. 84—85°, and the β -(*anti*-)form in needles, m. p. 71°. The α -modification is readily transformed by chlorine into the more stable β -form.

Methyl chloroimino-p-toluate, $\text{C}_6\text{H}_4\text{Me} \cdot \text{C}(\text{OMe})\text{NCl}$, is a colourless oil.

Methyl chloroimino- β -naphthoate, $\text{C}_{10}\text{H}_7 \cdot \text{C}(\text{OMe})\text{NCl}$, prepared by chlorinating methyl imino- β -naphthoate, is separated into the two modifications by adding light petroleum to its chloroform solution. The α -form is precipitated in minute crystals, m. p. 125°, and from the filtrate is obtained the β -form in large, thin plates, m. p. 72°. By heating with water, each modification is partly transformed into the other, probably by the action of a trace of hypochlorous acid or chlorine liberated from the chloroimino-ester.

Ethyl chloroimino- β -naphthoate (Slosson, Abstr., 1903, i, 475), when prepared by the hypochlorous acid method, yields an α -(*syn*-)variety, m. p. 72°, and a substance crystallising in needles, m. p. 39°, which is probably a mixture of both forms.

Methyl chloroimino-p-bromobenzoate, $\text{C}_6\text{H}_4\text{Br} \cdot \text{C}(\text{OMe})\text{NCl}$, crystallises in plates and needles, m. p. 60°; it does not, however, occur in

two stereoisomeric modifications. *Methyl chloroimino-p-bromo-m-nitrobenzoate*, $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{C}(\text{OMe}) \cdot \text{NCl}$, also crystallises in plates and needles, m. p. 95° , which are not stereoisomeric. *Methyl chloroimino-p-anisate*, $\text{MeO} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{OMe}) \cdot \text{NCl}$, prepared from *methyl iminoanisate hydrochloride*, is a pale yellow oil with a sharp odour.

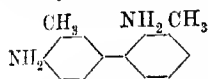
Methyl bromoimino-m-nitrobenzoate, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{OMe}) \cdot \text{NBr}$, prepared from methyl imino-*m*-nitrobenzoate and hypobromous acid, crystallises in plates, m. p. 99.5° , and needles, m. p. 101° , which are not stereoisomeric. *Methyl bromoimino- β -naphthoate*,
 $\text{C}_{10}\text{H}_7 \cdot \text{C}(\text{OMe}) \cdot \text{NBr}$,

has m. p. $99-100^\circ$.

J. C. C.

The Transformation of Hydrazotoluene into Tolidine.
 J. P. VAN LOON (*Chem. Weekblad*, 1908, 5, 689-698).—The transformation of hydrazotoluene into tolidine has been investigated quantitatively, and it has been found that 100 grams of hydrazotoluene yield

87.4 grams of tolidine, 2 grams of azotoluene, and 2 grams of toluidine. A small proportion of an isomeric tolidine, probably of the annexed formula, is also formed, but has not been obtained free from tolidine. The estimation of the tolidine was effected by precipitation as sulphate from hydrochloric acid solution by magnesium sulphate, a correction being necessary on account of tolidine sulphate being appreciably soluble in cold water. The value of the correction factor was ascertained by experiments on the solubility of the sulphate at certain temperatures.



A. J. W.

Replacement of Hydroxyl Groups by Hydrazino-groups.
 HARTWIG FRANZEN and TH. EICHLER (*J. pr. Chem.*, 1908, [ii], 78, 157-164. Compare Abstr., 1905, i, 244, and following abstract).—It has not been found possible to replace the hydroxyl groups in catechol and quinol by hydrazino-residues, or yet to transform 1:3:4-tolylene-diamine into the corresponding hydrazine derivative.

Dibenzylidene-1:3-phenylenedihydrazine, $\text{C}_6\text{H}_4(\text{NH} \cdot \text{N} \cdot \text{CHPh})_2$, obtained by the action of benzaldehyde on the crude product obtained by heating resorcinol, hydrazine sulphate, and a 50% solution of hydrazine hydrate for six hours to $110-120^\circ$ in an atmosphere of hydrogen, crystallises from xylene and has m. p. $247-248^\circ$.

Pyruvic acid reacts with the same condensation product, yielding *dipyrvic acid-m-phenylenedihydrazine*, $\text{C}_6\text{H}_4(\text{NH} \cdot \text{N} \cdot \text{CMe} \cdot \text{CO}_2\text{H})_2$, in the form of a yellow solid, m. p. 191° .

Hydrazine salicylate, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H} \cdot \text{N}_2\text{H}_4$, forms colourless crystals, m. p. 106° , which, when heated by means of nitrobenzene vapour, yield 3-keto-1:3-dihydroindazole (Fischer, Abstr., 1882, 1068). Salicylhydrazide when heated in the same manner yields the indazole in addition to *disalicylhydrazide*, $\text{N}_2\text{H}_4(\text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{OH})_2$, m. p. 301° .

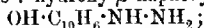
Hydrazine-o-hydroxytoluate, $\text{OH} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CO}_2\text{H} \cdot \text{N}_2\text{H}_4$ [Me:OH:CO₂H = 1:2:3], has m. p. $133-134^\circ$; the isomeric *meta*-compound [1:3:4] $137-138^\circ$, and the *para*-compound [1:4:3], 130° . When these salts are heated, they yield mixtures of hydrazino- and dihydroindazole derivatives, which so far have not been separated.

β -Hydroxynaphthoic acid hydrazide, $\text{OH} \cdot \text{C}_{10}\text{H}_6 \cdot \text{CO} \cdot \text{NH} \cdot \text{NH}_2$ [2:3],

crystallises from alcohol in yellow plates, m. p. 203—204° (decomp.), and yields a *benzylidene* derivative, $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CHPh}$, m. p. 224.5°.

J. J. S.

7-Hydroxy- β -naphthylhydrazine. HARTWIG FRANZEN and W. DEIBEL (*J. pr. Chem.*, 1908, [ii], 78, 143—157).—Although 2:3-dihydroxynaphthalene yields 2:3-naphthylenedihydrazine when heated with hydrazine hydrate, the isomeric 2:7-dihydroxy-derivative, under similar conditions, yields 7-hydroxy- β -naphthylhydrazine,

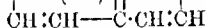


even when the latter compound is heated with hydrazine hydrate, a good yield of the dihydrazine derivative is not obtained.

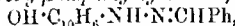
This anomalous behaviour of the 2:7-dihydroxynaphthalene cannot be explained by supposing that one of the hydroxyl groups reacts as the tautomeric ketone, since ketones also condense readily with hydrazine.

The best yield of 7-hydroxy- β -naphthylhydrazine is obtained when the dihydroxy-derivative, hydrazine sulphate, and a 45% solution of hydrazine hydrate are heated at 120—125° for eight hours in an atmosphere of hydrogen. It crystallises from water or alcohol in colourless plates, m. p. 176° (decomp.), and, when exposed to the air, turns red. It dissolves in acids, but not in alkalis or ether. The *hydrochloride*, $\text{C}_{10}\text{H}_6\text{ON}_2\cdot\text{HCl}$, is readily soluble in water, and has m. p. 192°; the *sulphate* is somewhat less soluble, and has m. p. 231° (decomp.); the *nitrate* has m. p. 173° (decomp.), and also decomposes when kept for some time. When the finely-divided base, obtained by the addition of a little potassium hydroxide solution to its aqueous solution, is oxidised by aspirating air through the suspension, a dark red solution is formed, and this yields a red precipitate with carbon dioxide.

Nitrous acid transforms the base into a *dinitroso*-derivative, probably $\text{OH}\cdot\text{CH}\cdot\text{C}(\text{NO})\cdot\text{C}\cdot\text{CH}\cdot\text{C}(\text{NO})\cdot\text{NH}_2$; it has m. p. 124°.



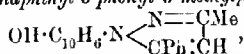
Benzaldehyde 7-hydroxy- β -naphthylhydrazine,



crystallises from benzene in pale yellow plates, m. p. 233°. The corresponding *o*-hydroxybenzaldehyde derivative, $\text{C}_{17}\text{H}_{14}\text{O}_2\text{N}_2$, has m. p. 223°.

7-Hydroxy- β -naphthylsemicarbazide, $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, obtained by the action of a concentrated aqueous solution of potassium cyanate on the hydrazine derivative, crystallises from alcohol in reddish-violet needles, m. p. 228°. 7-Hydroxy- β -naphthylphenylthiosemicarbazide, $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{NH}\cdot\text{NH}\cdot\text{CS}\cdot\text{NHPh}$, obtained by the action of phenylthiocarbimide on the hydrazine, has m. p. 183°.

The base condenses with an alcoholic solution of benzoylacetone, yielding 7'-hydroxy- β -naphthyl-5-phenyl-3-methylpyrazole,



m. p. 199°, and with ethyl acetoacetate, yielding 7'-hydroxy- β -naphthyl-

3-methylpyrazolone, $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{N} < \begin{array}{c} \text{N}=\text{CMe} \\ | \\ \text{CO}\cdot\text{CH}_2 \end{array}$, m. p. 243°.

7-Chloro- β -naphthol, $C_{10}H_6Cl \cdot OH$, can be prepared by dropping a hot solution of the hydroxyhydrazine into a boiling solution of copper sulphate; it crystallises from light petroleum in colourless plates, m. p. 126.5° . The corresponding acetyl derivative, $C_{10}H_6Cl \cdot OAc$, crystallises from toluene in colourless plates, m. p. 104.5° .

An acetic acid solution of the hydroxyhydrazine is oxidised by copper sulphate solution to β -naphthol.

7-Amino- β -naphthol, $OH \cdot C_{10}H_6 \cdot NH_2$, obtained together with 2:7-naphthylenediamine by heating 2:7-dihydroxynaphthalene with ammonium sulphite and hydroxide in a reflux apparatus, has m. p. 201° .

In the preparation of 7-hydroxy- β -naphthylhydrazine, a small amount of 2:7-naphthylenedihydrazine is formed. This yields a dibenzylidene derivative, $C_{10}H_6(NH \cdot N \cdot CHPh)_2$, m. p. 186.5° .

7-Amino- β -naphthylhydrazine, $NH_2 \cdot C_{10}H_6 \cdot NH \cdot NH_2$, obtained by the action of hydrazine hydrate and sulphate on 2:7-naphthylenediamine, has m. p. 184° , and yields a dibenzylidene derivative,

$CHPh \cdot N \cdot C_{10}H_6 \cdot NH \cdot N \cdot CHPh$,
m. p. 201.5° , and a di-*o*-hydroxybenzylidene derivative,
 $OH \cdot C_6H_4 \cdot CH \cdot N \cdot C_{10}H_6 \cdot NH \cdot N \cdot CH \cdot C_6H_4 \cdot OH$,

which begins to decompose at 169° .

J. J. S.

Action of Nitrogen Peroxide on Aldehyde Phenylhydrazones. ROBERTO CIUSA and UGO PESTALOZZA (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 840—846).—The action of nitrogen peroxide on aldehyde phenylhydrazones in ethereal solution yields the corresponding arylnitroformaldehyde phenylhydrazones in almost quantitative proportions: $CHAr \cdot N_2HPh \rightarrow NO_2 \cdot CAr \cdot N_2HPh$, small amounts of free aldehyde, diazobenzene nitrate, and oxidation products being also formed. The reaction affords a very convenient method of preparing arylnitroformaldehyde phenylhydrazones, being easier to carry out, and giving better yields of purer material, than the action of diazobenzene salts on the primary nitrohydrocarbons, or the action of nitrous acid on the phenylhydrazones. As regards the mechanism of the reaction, the nitro-group replaces the methinic hydrogen atom, a further proof being thus afforded of the peculiar activity of this hydrogen atom.

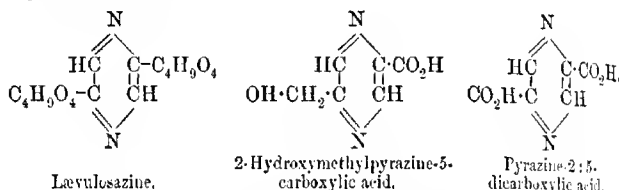
The phenylhydrazones on which the reaction was tried were those of benzaldehyde, *m*-nitrobenzaldehyde, anisaldehyde, and piperonal. The compound obtained in the last case was *nitromethylenedioxy- ω -benzaldehydophenylhydrazone*, $CH_2O_2 \cdot C_6H_3 \cdot C(NO_2) \cdot N_2HPh$, which crystallises from a mixture of benzene and alcohol in ruby-red, prismatic needles, m. p. 119° , and dissolves in concentrated sulphuric acid, giving a violet coloration changing to red, and with alkalis, forming dark red solutions, from which it is re-precipitated by the addition of acid; the potassium salt is obtained as a golden-yellow, crystalline powder.

T. H. P.

The Degradation of Lævulosazine (Ditetrahydroxybutyl-pyrazine) in the Animal Body. KARL STOLTE (*Biochem. Zeitsch.*, 1908, 12, 499—509).—After ingestion of lævulosazine, a product is

excreted in the urine which gives with ferrous sulphate in acetic acid solution a carmine-red colour.* The substance causing this reaction was isolated from rabbits' urine by concentrating it to a syrup and precipitating the inorganic salts with alcohol. On addition of a concentrated aqueous solution of copper acetate acidified with acetic acid, a copper salt was precipitated. This was dissolved in sodium hydroxide solution and decomposed by hydrogen sulphide, the filtrate from the sulphide decolorised by charcoal, and copper acetate in aqueous solution added. A crystalline precipitate was thereby obtained, which was identified as the copper salt of 2-hydroxymethylpyrazine-5-carboxylic acid. On oxidation with hydrogen peroxide in alkaline solution, it yielded pyrazine-2:5-dicarboxylic acid, m. p. 272—273°.

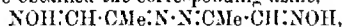
The relation of levulosazine to these degradation products can be expressed as follows:



The constitution of the excreted product was also confirmed by the preparation of an acetyl derivative. The substance which sometimes in normal urine gives a red coloration with ferrous sulphate is not a pyrazine derivative.

S. B. S.

Preparation of Certain Azines. GIACOMO PONZIO and R. GIOVETTI (*Gazzetta*, 1908, 38, ii, 123—126; *Atti R. Accad. Sci. Torino*, 1908, 43, 817—820).—The conclusion drawn by von Rothenburg (*Abstr.*, 1893, i, 701), that when hydrazine acts on compounds containing the group :NOH the latter is always replaced by :N·NH₂, is inaccurate. Thus, from isonitrosoacetone and hydrazine, the authors have obtained the corresponding azine,



and from the latter, by means of a simple and general reaction, the azines of mixed isonitroso-ketones, $\text{Me}\cdot\text{CO}\cdot\text{CAr}\cdot\text{NOH}$, which cannot be prepared directly. The latter compounds crystallise well, and are converted into mixed diketones, $\text{CH}_3\cdot\text{CO}\cdot\text{CO}\cdot\text{Ar}$, by the action of dilute acids, but are not transformable into pyrazolines.

isoNitrosoacetoneazine, $\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4$, prepared by the action of powdered hydrazine sulphate (1 mol.) on a solution of isonitrosoacetone (2 mols.) in 20% sodium hydroxide solution, separates from alcohol or water in crystals, m. p. 221° (decomp.).

isoNitrosophenylglucetoneazine, $(\text{NOH}\cdot\text{CPh}\cdot\text{CMe})_2\text{N}_2$, obtained by the interaction of isonitrosoacetoneazine and diazobenzene chloride (2 mols.) in 10% sodium hydroxide solution, crystallises from alcohol in yellowish-red needles, m. p. 187—188°, and yields hydrazine sulphate and phenyl methyl diketone when heated with 10% sulphuric acid.

iso. *Nitroso-p-tolylacetoneazine*, $[C_6H_4Mo \cdot C(NO) \cdot CMe]_2N_2$, prepared by treating isonitrosoacetoneazine in alkaline solution with diazo-*p*-toluene chloride, crystallises from alcohol in yellow laminæ, m. p. 198—199° (decomp.).

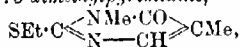
iso. *Nitrosoanisylacetoneazine*, $[OMe \cdot C_6H_4 \cdot C(NO) \cdot CMe]_2N_2$, prepared in a similar manner to the preceding compounds, crystallises from alcohol in yellow prisms, m. p. 193—194° (decomp.), and yields hydrazine sulphate and *p*-anisyl methyl diketone, m. p. 44—45°, when distilled with 10% sulphuric acid. T. H. P.

Pyrimidines. XXXIII. Synthesis of *N*-Alkyl Derivatives of Cytosine, Thymine, and Uracil. TREAT B. JOHNSON and SAMUEL H. CLAPP (*J. Biol. Chem.*, 1908, 5, 49—70. Compare this vol., i, 692, 693).—Various *N*-alkyl derivatives of cytosine, thymine, and uracil have been synthesised on account of the occurrence of certain methyl-purines in nature, and also on account of the relationship between methyluracils and the purines, theobromine and caffeine.

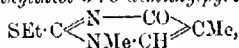
The introduction of methyl groups into these pyrimidine derivatives has a similar influence on their physical properties to that on the purines. They increase the solubility and lower the melting points. The 3-methyl pyrimidines melt at higher temperatures than the isomeric 1-methyl derivatives.

When 6-oxy-2-ethylthiol-5-methylpyrimidino is methylated by means of methyl iodide and alcoholic potassium hydroxide, a mixture of the two isomeric 1:5- and 3:5-dimethyl derivatives is obtained.

6-Oxy-2-ethylthiol-1:5-dimethylpyrimidine,

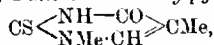


is less soluble, and crystallises from water in long, slender prisms, m. p. 65°. 6-Oxy-2-ethylthiol-3:5-dimethylpyrimidine,



crystallises from benzene in colourless prisms, m. p. 156°. When hydrolysed with hydrobromic acid, each thio-derivative yields the corresponding thymine.

1-Methylthymine, $CO \begin{array}{c} \diagup NMe \cdot CO \\ \diagdown NH-CH \end{array} > CMe$, crystallises from water in stout prisms, m. p. 202—205° (decomp.), and the isomeric 3-methylthymine crystallises from the same solvent in prismatic needles or octahedral prisms, m. p. 280—282°. In the formation of the latter compound, a certain amount of 6-oxy-2-thio-3:5-dimethylpyrimidine,



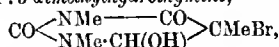
is also formed; it is less soluble in water than the methylthymine, and crystallises in needles, m. p. 229—230°.

Bromine water converts 1-methylthymine into 5-bromo-4-hydroxy-1-methylhydrothymine, $CO \begin{array}{c} \diagup NMe-CH \\ \diagdown NH-CH(OH) \end{array} > CMeBr$, which crystallises in stout prisms, m. p. 123—125°, when heated slowly. The corresponding 5-nitro-derivative, $C_6H_6O_3N_3$, obtained by the action of nitric acid on the base, forms well-developed prisms, m. p. 135—136° (decomp.).

The isomeric *5-nitro-4-hydroxy-3-methylhydrothymine*, obtained by the action of nitric acid on 3-methylthymine, crystallises in large prisms, which decompose at 178—181°.

The *monopotassium* derivative of thymine, $C_5H_5O_2N_2K$, crystallises from alcohol in long needles.

1:3-Dimethylthymine (Stendel, Abstr., 1901, i, 108) is most readily obtained by methylating thymine, and with bromine water yields *5-bromo-4-hydroxy-1:3-dimethylhydrothymine*,



in the form of prisms, m. p. 132—133°.

Monopotassiumuracil, obtained by digesting uracil with the theoretical amount of alcoholic potassium hydroxide, has the composition $C_4H_3O_2N_2K \cdot H_2O$, and loses its water of hydration at 120°. When uracil is methylated in the presence of potassium hydroxide,

1:3-dimethyluracil, $CO \begin{array}{c} \text{NMe} \text{---} \text{CO} \\ \diagup \quad \diagdown \\ \text{NMe} \cdot \text{CH} \end{array} \text{CH}$, which crystallises from a mixture of ether and alcohol in long, slender prisms, m. p. 121—122°, is obtained. With bromine water this base yields *5-dibromo-4-hydroxy-*

1:3-dimethylhydrouracil, $CO \begin{array}{c} \text{NMe} \text{---} \text{CO} \\ \diagup \quad \diagdown \\ \text{NMe} \cdot \text{CH}(\text{OH}) \end{array} \text{CBr}_2$, m. p. 135—136°, which is transformed into *5-bromo-1:3-dimethyluracil* when digested with alcohol.

3-Methylcytosine, $CO \begin{array}{c} \text{N}=\text{C}(\text{NH}_2) \\ \diagup \quad \diagdown \\ \text{NMe} \text{---} \text{CH} \end{array} \text{CH}$, obtained by methylating cytosine, crystallises from methyl alcohol in prisms, decomp. 278—279°. The *platinichloride*, $(C_5H_7ON_3)_2H_2PtCl_6 \cdot 2H_2O$, crystallises in slender prisms, and the *picrate* in long prisms, which decompose at 280° when heated slowly. *5-Bromo-3-methyluracil*, $C_5H_5O_2N_2Br$, obtained by treating 3-methylcytosine with bromine and water and digesting the product with ethyl alcohol, crystallises from water in slender needles, which decompose at 255—260°.

2-Oxy-6-phenylmethylaminopyrimidine, $CO \begin{array}{c} \text{N}:\text{C}(\text{NPhMe}) \\ \diagup \quad \diagdown \\ \text{NH} \text{---} \text{CH} \end{array} \text{CH}$, obtained by the action of methylaniline on 6-chloro-2-ethylthiopyrimidine and digesting the product with hydrobromic acid, crystallises from alcohol in hexagonal plates, which do not decompose below 285°. When this base is methylated, it yields 2-oxy-6-phenylmethylamino-3-methylpyrimidine, $CO \begin{array}{c} \text{N}:\text{C}(\text{NPhMe}) \\ \diagup \quad \diagdown \\ \text{NMe} \text{---} \text{CH} \end{array} \text{CH}$, which crystallises in striated prisms, m. p. 186—187°.

3:5-Dimethylecyto-ine, $CO \begin{array}{c} \text{N}:\text{C}(\text{NH}_2) \\ \diagup \quad \diagdown \\ \text{NMe} \text{---} \text{CH} \end{array} \text{CMe}$, obtained by methylating 5-methylcytosine (Abstr., 1904, i, 624), crystallises from methyl alcohol in prisms, which decompose at 300—310°.

The formation of the 3-methylthymine by dissolving 3:5-dimethylcytosine in concentrated bromine water, evaporating to dryness, and digesting the product with absolute alcohol, establishes the positions of the methyl groups in 3:5-dimethylecytosine.

[With N. A. MARTIN.]—Electrical conductivity measurements have

been made with thymine and its *N*-methyl derivatives. The conductivities tend to increase with the length of time the solutions are kept, especially in the case of 1- and 3-methylthymines. J. J. S.

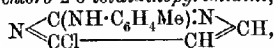
Pyrimidines. XXXV. Action of Potassium Thiocyanate on Some Imide Chlorides. TREAT B. JOHNSON and WALTER F. STORREY (*Amer. Chem. J.*, 1908, 40, 131—147).—Wheeler and Bristol (Abstr., 1905, i, 483) have shown that 6-chloro-2-ethylthiopyrimidine, 6-chloro-2-ethylthiol-5-methylpyrimidino, and 6-chloro-5-bromo-2-ethylthiopyrimidine give thiocarbimido-derivatives when treated with potassium thiocyanate, but the intermediate formation of thiocyanates was not observed. Johnson and McCollum, however (Abstr., 1906, i, 768), found that 6-chloro-5-ethoxy-2-ethylthiopyrimidine yields the 6-thiocyano-derivative, which can be transformed into the corresponding 6-thiocarbimido-derivative. The present authors have now examined the behaviour of potassium thiocyanate towards 6-chloro-2-*p*-toluidinopyrimidine, 6-chloro-2-*o*-toluidinopyrimidine, and 6-chloro-2-*p*-tolyl-4-methylpyrimidine; the two forms do not react with potassium thiocyanate, but the latter gives the corresponding thiocyano-derivative, which can be transformed into the isomeric thiocarbimido compound. Moreover, the substances examined by Wheeler and Bristol yield thiocyano-derivatives, readily transformed into the thiocarbimido-isomerides when the time of the reaction is limited to twenty to sixty minutes, instead of three to fifteen hours, as employed by these authors.

[With ELMER V. MCCOLLUM.]—6-Thiocyano-2-ethylthiopyrimidine, $N \begin{smallmatrix} \text{C(SET)} \\ \text{C(SCN)} \end{smallmatrix} \begin{smallmatrix} =N \\ \cdot CH \end{smallmatrix} \gg CH$, prepared by warming 6-chloro-2-ethylthiopyrimidine with potassium thiocyanate in acetone or 95% alcoholic solution, crystallises from alcohol in aggregates of rectangular prisms, m. p. 82°. On heating at 80—90° for four to five hours, it is transformed into the thiocarbimido-derivative. This is obtained as a yellow oil, b. p. 200—205°/45—50 mm., which, after some time, deposits a yellow, crystalline compound, m. p. 175—177°. This does not react with ammonia, and is regarded as a polymeric form of 2-ethylthiol-6-thiocarbimidopyrimidine (compare Wheeler and Bristol, *loc. cit.*).

6-Thiocyano-2-ethylthiol-5-methylpyrimidine, $N \begin{smallmatrix} \text{C(SET)} \\ \text{C(SCN)} \end{smallmatrix} \begin{smallmatrix} =N \\ \cdot CMe \end{smallmatrix} \gg CH$, crystallises from alcohol in prisms, m. p. 95°. It dissolves in thioacetic acid, forming prismatic crystals, m. p. 179—180°, which probably consist of 6-thio-2-ethylthiol-5-methylpyrimidine. 5-Bromo-6-thiocyano-2-ethylthiopyrimidine, $N \begin{smallmatrix} \text{C(SET)} \\ \text{C(SCN)} \end{smallmatrix} \begin{smallmatrix} =N \\ \cdot CBr \end{smallmatrix} \gg CH$, crystallises from alcohol in prisms, m. p. 81—82°. With thioacetic or thiobenzoic acid, it yields 5-bromo-6-thio-2-ethylthiopyrimidine, and, when heated for two hours at 150—160°, it is transformed into the thiocarbimido-isomeride.

6-Oxy-2-*o*-toluidinopyrimidine, $NH \begin{smallmatrix} \text{C(NH} \cdot C_6H_4Me) \\ \text{CO} \end{smallmatrix} \begin{smallmatrix} =N \\ \cdot CH \end{smallmatrix} \gg CH$, prepared by heating a mixture of 6-oxy-2-ethylthiopyrimidine and *o*-toluidine for three days on the steam-bath, separates from alcohol or

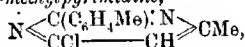
acetic acid in prismatic crystals, m. p. 219—220°. With phosphoryl chloride, it yields 6-chloro-2-o-toluidinopyrimidine,



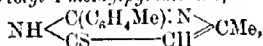
separating from alcohol in crystals, m. p. 78°, which, when heated with alcoholic ammonia, furnishes 6-amino-2-o-toluidinopyrimidine, crystallising from alcohol in small prisms, m. p. 124°, and when boiled with a benzene solution of aniline gives 6-anilino-2-o-toluidinopyrimidine, crystallising from alcohol in hexagonal plates, m. p. 128°; the hydrochloride forms slender needles, m. p. 126°.

6-Oxy-2-p-toluidinopyrimidine, prepared from 6-oxy-2-ethylthiolpyrimidine and p-toluidine, crystallises from acetic acid in needles, m. p. 270—271°. With phosphoryl chloride, it gives 6-chloro-2-p-toluidinopyrimidine, separating from alcohol in prisms, m. p. 112—113°. This reacts with aniline, yielding 6-anilino-2-p-toluidinopyrimidine, which crystallises from alcohol in needles, m. p. 135°; the hydrochloride forms prisms, decomposing at 134°. 6-Oxy-2-β-naphthylaminopyrimidine, prepared from β-naphthylamine and 6-oxy-2-ethylthiolpyrimidine, crystallises from alcohol in needles, m. p. 270°.

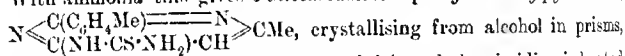
6-Chloro-2-p-tolyl-4-methylpyrimidine,



prepared by heating a mixture of 6-oxy-2-p-tolyl-4-methylpyrimidine, phosphorus pentachloride, and phosphoryl chloride, crystallises from alcohol in prisms, m. p. 107°. With potassium thiocyanate, this gives 6-thiocyano-2-p-tolyl-4-methylpyrimidine, separating from alcohol in fern-like crystals, m. p. 123°, which, when warmed with thiobenzoic acid, yields 6-thio-2-p-tolyl-4-methylpyrimidine,



crystallising from alcohol in slender prisms, m. p. 114°. When the thiocyanate compound is heated for two and a-half hours at 130—135°, it undergoes re-arrangement, yielding prisms, m. p. 207—208°, which probably consist of a polymeric form of the thiocarbimido-derivative. With ammonia this gives 6-thiocarbamido-2-p-tolyl-4-methylpyrimidine,



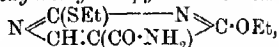
crystallising from alcohol in prisms, m. p. 145—146°. When 6-chloro-2-p-tolyl-4-methylpyrimidine is heated with ammonia at 180—190° for two hours, it yields 6-amino-2-p-tolyl-4-methylpyrimidine, separating from alcohol in hexagonal tablets, m. p. 178—179°, and, when warmed with a benzene solution of aniline, 6-anilino-2-p-tolyl-4-methylpyrimidine, crystallising from alcohol in needles, m. p. 120—121°, is obtained; the hydrochloride separates from alcohol in clusters of needles, m. p. 269—270° (decomp.).

J. C. C.

Pyrimidines. XXXVI. Synthesis of Cytosine-5-carboxylamide. HENRY L. WHEELER and CARL O. JOHNS (*Amer. Chem. J.*, 1908, 40, 233—251. Compare *Abstr.*, 1907, i, 559, 1083).—The authors have previously shown that ethyl-ψ-thiocarbamide and ethyl ethoxymethylene malonate condense to form ethyl 2-ethylthiol 6-oxy-

pyrimidine-5-carboxylate, and that the corresponding acid is readily obtained from this. They have now succeeded in greatly increasing the yield of pyrimidine in this condensation, and have made it the starting point for further syntheses.

The acid chloride of 6-chloro-2-ethylthiopyrimidine-5-carboxylic acid, $\text{N} \begin{smallmatrix} \text{C}(\text{SEt}) \text{---} \text{N} \\ \text{CH:C}(\text{COCl}) \end{smallmatrix} \text{CCl}$, prepared by boiling the dry oxy-acid with phosphoryl chloride, separates from light petroleum in radiating clusters of colourless prisms, m. p. 38—40°. With cold aqueous ammonia, the corresponding amide, $\text{N} \begin{smallmatrix} \text{C}(\text{SEt}) \text{---} \text{N} \\ \text{CH:C}(\text{CO}\cdot\text{NH}_2) \end{smallmatrix} \text{CCl}$, is formed, which separates from benzene in long, hair-like crystals, m. p. 134°, and with sodium ethoxide yields 6-ethoxy-2-ethylthiopyrimidine-5-carboxylamide,

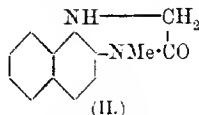
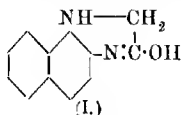


m. p. 134°. When the acid chloride of 6-chloro-2-ethylthiopyrimidine-5-carboxylic acid is warmed with aqueous ammonia, 6-amino-2-ethylthiopyrimidine-5-carboxylamide, $\text{N} \begin{smallmatrix} \text{C}(\text{SEt}) \text{---} \text{N} \\ \text{CH:C}(\text{CO}\cdot\text{NH}_2) \end{smallmatrix} \text{C}\cdot\text{NH}_2$, stout prisms, m. p. 218—219°, is produced; with bromine, it yields a dibromo-additive compound. When the latter is heated until the loss corresponds with the weight of one molecular proportion of hydrogen bromide, the resulting material dissolved in dilute potassium hydroxide, and the solution acidified with acetic acid, cytosine-5-carboxylamide,

$\text{N} \begin{smallmatrix} \text{CO} \text{---} \text{NH} \\ \text{C}(\text{NH}_2)\cdot\text{C}(\text{CO}\cdot\text{NH}_2) \end{smallmatrix} \text{CH}$, is obtained. This is also formed, together with the acid, by the action of hydrochloric acid on 6-amino-2-ethylthiopyrimidine-5-carboxylamide; it does not melt at 310°. The substance previously regarded as having this constitution (*loc. cit.*, 1053) was probably impure or partly hydrated cytosine. On hydrolysis with hydrochloric acid, it yields cytosine-5-carboxylic acid, and it forms the following salts: *hydrochloride*, colourless, stout, pointed prisms; *nitrate*, truncated octahedrons or tufts of short hairs; *sulphate*, pearly scales; and *picrate*. J. C. C.

Preparation of 2-Hydroxydihydro- and 1-Alkyl-2-ketodihydro-quinoxalines. MARTIN LANGE (D.R.-P. 196563).—The *o*-nitrosophenols interact with aldehydes and primary amines or with Schiff's bases to form quinoxaline derivatives.

2-Hydroxydihydro-1': 2'-naphthaquinoxaline (I), a yellow, sandy



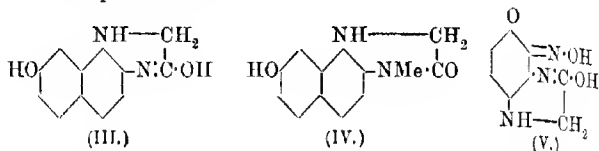
powder, m. p. 240°, is produced by adding acetaldehyde and ammonium chloride to an alkaline solution of 1-nitroso- β -naphthol.

2-Keto-1-methyldihydro-1': 2'-naphthaquinoxaline (II), m. p. 155.5°, is obtained by substituting methylamine hydrochloride for ammonium

chloride in the foregoing reaction. The corresponding 2-keto-1-ethylidihydro-1':2'-naphthaquinoxaline, m. p. 164°, is produced by condensing 1-nitroso- β -naphthol with 30% ethylamine and acet. aldehyde.

The patent contains a description of several other quinoxalines derived from 1-nitroso- β -naphthol, 2-nitroso- α -naphthol, and their carb. oxylic and sulphonic acids, and, in addition, two obtained from nitroso-2:7-dihydroxynaphthalene and one from dinitrosoresorcinol.

These compounds have the formulæ:



(III) and (IV) are obtained from 2:7-dihydroxynaphthalene, acetaldehyde, and ammonia, or methylamine, respectively.

(V), which is produced from dinitrosoresorcinol, acetaldehyde, and ammonia, separates in orange crystals.

G. T. M.

Ethyl Pyromucylacetate [Furfuroylacetate]. II. 3-Furyl-5-pyrazolone. HENRY A. TORREY and JOAQUIN E. ZANETTI (*J. Amer. Chem. Soc.*, 1908, **30**, 1241—1244).—When ethyl furfuroylacetate is treated with phenylhydrazine, it is converted into 1-phenyl-3-furyl-5-pyrazolone. This compound and some of its derivatives have been described previously (Abstr., 1907, i, 146).

By the action of hydrazine on ethyl furfuroylacetate, 3-furyl-5-pyrazolone, $\begin{array}{c} \text{CH}_3\text{O} \\ | \\ \text{CH}_2\text{CH} \end{array} > \text{C} \cdot \text{C} < \begin{array}{c} \text{CH}_2\text{CO} \\ | \\ \text{N} \end{array} \text{NH}$, m. p. 223° (decomp.), is obtained, and forms small, rectangular plates. The *picrate* decomposes at 192°. The *acetyl* derivative, m. p. 153—154°, and the *diacetyl* derivative, m. p. 102°, crystallise in long, white needles. The *benzylidene* derivative forms a light brown, amorphous powder, and does not melt at 300°. When the pyrazolone is treated with phenylcarbimide, a compound, probably 3-furyl-5-pyrazolonephenylcarbamide,

$\begin{array}{c} \text{H}_2\text{C} \cdot \text{CO} \\ | \\ \text{C}_4\text{H}_3\text{O} \cdot \text{C} \end{array} = \text{N} > \text{N} \cdot \text{CO} \cdot \text{NHPh}$, m. p. 192°, is obtained in the form of small, white needles.

E. G.

Trihydroxymethyldihydrouracil. ROBERT BEHREND and KARL BEER (*Annalen*, 1908, **362**, 115—122. Compare Behrend and Grünewald, Abstr., 1902, i, 834).—A further account of the properties of α - and β -trihydroxymethyldihydrouracils (compare Behrend and Osten, Abstr., 1906, i, 309). Both of these compounds crystallise with 1H₂O. The compound obtained by the interaction of the β -compound and phenylhydrazine is a *phenylhydrazone*, C₁₁H₁₁O₄N₄, since it liberates phenylhydrazine when treated with alkali. Both α - and β -trihydroxymethyldihydrouracils are oxidised by potassium permanganate in the presence of potassium hydrogen carbonate, yielding *potassium acetoxalurate*, C₅H₅O₅N₂K, 2H₂O, crystallising in needles

decomposing at 214—216°. An *acid salt*, $C_5H_5O_3N_2K \cdot C_5H_6O_5N_2$, m. p. 201°, separates when a solution of the neutral salt is acidified with hydrochloric acid.

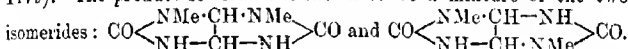
The α -uracil when heated at 105—110° loses $2H_2O$, yielding a yellow powder which decomposes at 140—145°. The β -uracil also loses $2H_2O$ at 105—110°, yielding a syrupy acetylallanturic acid. The same acid is also formed when a neutral or slightly alkaline aqueous solution of either the α - or β -uracil is warmed. A *phenylhydrazone*, $C_{11}H_{12}O_3N_4$, forming yellow crystals decomposing at 219—220°, was prepared.

Acetylallanturic acid is oxidised by potassium permanganate in the presence of potassium hydrogen carbonate to oxaluric acid and acetic acid; in no case was either acetoxaluric acid or acetylcarbamide formed.

W. H. G.

Dimethylglycoluril and β -Methylhydantoin. EMIL WEITZNER (*Annalen*, 1908, 362, 125—131).—An account of attempts to obtain a fruitful and simple method for preparing β -methylhydantoin.

Methylcarbamide, or, better, its acetyl derivative, reacts with glyoxal in aqueous solution in the presence of hydrochloric acid, yielding dimethylglycoluril (compare Franchimont and Klobbie, *Abstr.*, 1888, 1179). The product so formed is shown to be a mixture of the two isomerides:



Both these compounds when decomposed with hydrochloric acid yield the same product, namely, a mixture of α - and β -methylhydantoin, which is separated only with great difficulty. The best method for obtaining β -methylhydantoin is by acting on sarcosine hydrochloride with potassium cyanate in aqueous solution, and heating the resulting solution with hydrochloric acid.

The mixture of isomeric *dimethylglycolurils* prepared from glyoxal and acetylmethylcarbamide may be separated by fractional crystallisation from water. Both isomerides crystallise in long, colourless needles, and melt at 285—287° and 230—232° respectively.

W. H. G.

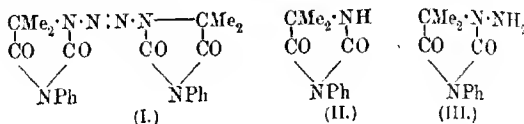
Preparation of Azoxy-derivatives. O. DIEFFENBACH (D.R.-P. 197714).—Azoxy-compounds may be conveniently obtained free from amines by digesting a mixture of a nitro-compound and hydrazo-derivative until they have interacted to furnish a mixture of azo- and azoxy-derivatives.

A mixture of azo- and azoxy-*o*-toluene is thus produced by maintaining a mixture of *o*-nitrotoluene, hydrazo-*o*-toluene, toluene, and aqueous sodium hydroxide (10%) at 90° for eight hours. Under similar conditions a mixture of *o*-nitrobenzoic acid and hydrazobenzeno yields sodium *o*-azoxybenzoate and azobenzene, which are readily separated. This reaction may be combined advantageously with the electrolytic production of hydrazo-derivatives.

The azoxy-compound is reduced electrolytically to a hydrazo-compound and then more nitro-compound is added, which is then reduced to the azoxy-compound by the hydrazo-derivative present, so that the nitro-

compound is being continuously reduced chemically whilst the electrolytic reduction is effected on the azoxy-derivative. G. T. M.

Hydantointetrazones. J. R. BAILEY (*J. Amer. Chem. Soc.*, 1908, 30, 1412—1418. Compare Abstr., 1904, i, 826).—The author adduces further evidence in favour of the constitution of the azo-hydantoin (*loc. cit.*) by showing the relation of azophenyldimethylhydantoin (I) to phenyldimethylhydantoin (II) and to aminophenyldimethylhydantoin (III).



1-Azo-3-phenyl-5:5-dimethylhydantoin after purification by crystallisation from ethyl acetoacetate decomposes at 285° (corr.), instead of 270° as given previously. When heated at 60° with sulphuric acid or boiled with alcoholic potash, it loses nitrogen and yields 3-phenyl-5:5-dimethylhydantoin, crystallising from water in prisms, m. p. 171° (corr.), which is also obtained by condensing phenylcarbimide with aminoisobutyronitrile and hydrolysing the product.

[With BARNEY BROOKS].—1-Amino-3-phenyl-5:5-dimethylhydantoin, m. p. 154.5° (corr.), is prepared by the action of dilute sulphuric acid on 1-carboxyisopropylamino-3-phenyl-5:5-dimethylhydantoin. It is oxidised with bromine water to 1-azo-3-phenyl-5:5-dimethylhydantoin. 1-Benzylideneamino-3-phenyl-5:5-dimethylhydantoin, prepared by heating aminophenyldimethylhydantoin with benzaldehyde or by heating phenylcarbimide with the benzylidenehydrazone of hydrazinoisobutyric acid, crystallises from alcohol in long, slender, pale yellow needles, m. p. 154° (corr.). J. C. C.

[Preparation of Diazo-derivatives of 1-Amino-β-naphthol-sulphonic Acids.] KALLE & Co. (D.R.-P. 195228 and 195322).—On adding aqueous sodium nitrite to a mixture of 1-amino-β-naphthol-4-sulphonic acid, zinc sulphate, and zinc hydroxide, diazotisation sets in, and is completed by heating at 40—55° for one or two hours. The diazo-derivative may be precipitated by the addition of acetic acid and sodium chloride. Other sulphonic acids of 1-amino-β-naphthol or 2-amino-α-naphthol may be diazotised in a similar manner.

The zinc salt may be replaced by the salts of magnesium, cobalt, nickel, and manganese, and, in general, by metallic salts of neutral reaction which are highly dissociated in aqueous solution. G. T. M.

The Extractives of Muscular Tissue. Relationship of Oblitine to Carnitine. R. KIMBERG (*Zeitsch. physiol. Chem.*, 1908, 56, 417—424. Compare this vol., ii, 609).—When carnitine is evaporated several times with 96% alcohol and a little hydrochloric acid, a product is formed from which oblitine can be isolated in the form of its hydrochloride. Oblitine would thus appear to be the diethyl ester

of dicarnitine. The platinichloride has the formula $C_{18}H_{38}O_5N_2Cl_6Pt$, and not $C_{18}H_{40}O_5N_2Cl_6Pt$ (Kutscher). Since Kutscher in the isolation of oblitine used methods which would transform carnitine into oblitine, it is questionable whether this latter exists in muscle extract.

J. J. S.

Blood-pigment. IX. LEON MARCHLEWSKI (*Zeitsch. physiol. Chem.*, 1908, 56, 316—320. Compare this vol., i, 232).—A further investigation of the action of diazobenzene chloride on hæmopyrrole has shown that at least four, and probably five, products are formed. (a) A product, the hydrochloride of which crystallises in brown, monoclinic or triclinic needles, m. p. 233°. (b) Rhombic crystals, with a ruby-red colour and coppery lustre, m. p. 268°. (c) Green needles of a hydrochloride, m. p. above 300°. (d) Brown needles with a green shimmer of a hydrochloride, m. p. 185—186°. The chief product is usually (a); product (d) appears to be formed when the conditions are somewhat altered.

It is shown that treatment of hæmopyrrole with acid affects it in such a manner that the yield of product (a) is diminished, and is ultimately nil.

J. J. S.

Part Played by Alkali in the Hydrolysis of Proteins by Trypsin. T. BRAILSFORD ROBERTSON and C. L. A. SCHMIDT (*J. Biol. Chem.*, 1908, 5, 31—48).—The change in alkalinity during tryptic fermentation has been followed by means of the gas chain. It is found that when the total hydroxyl-ion concentration is greater than 10^{-6} , the changes in concentration can be expressed by a unimolecular formula, but that with lower concentrations the change can be represented by a bimolecular formula. These facts appear to be inconsistent with the view that the hydroxyl ions act as an accessory catalyst, but are in harmony with the view that the real catalyst is a hydrolysable compound of trypsin with sodium hydroxide or other base present in the system.

It is suggested that the equilibrium, as regards change in \bar{OH} concentrations, which is attained after some time is a "false" equilibrium depending on the sum of the relations between the protein, trypsin, and alkali. The proteins used were casein and protamine.

J. J. S.

Hydrolysis of Legumin from the Vetch. THOMAS B. OSBORNE and FREDERICK W. HEYL (*Amer. J. Physiol.*, 1908, 22, 423—432).—The general properties of vetch legumin are similar to those of the pea legumin described previously (Abstr., 1907, i, 806). On hydrolysis, the various amino-acids are found in somewhat different proportions; these differences are most marked in the case of valine, aspartic acid, and lysine, but some hesitation is felt in drawing conclusions that these are sufficient in the present state of our technique to warrant the assertion that the two proteins are different.

W. D. H.

Photomethæmoglobin. OTTO LEERS (*Biochem. Zeitsch.*, 1908, 12, 252—258).—When methæmoglobin solutions are exposed to sunlight,

the brown colour is, as Bock has shown, converted into a red colour, and the modification of the blood-pigment, termed photomethæmoglobin, is formed. Its spectrum shows great similarity with that of cyanohæmoglobin. Methæmoglobin was prepared by a variety of methods, and this was converted into photomethæmoglobin by treatment with potassium ferri-cyanide and exposure to sunlight. The same effect was also produced by sodium ferro- and ferri-cyanides and other cyano-compounds. The solutions thus obtained exhibit on concentration the characteristic hydrocyanic acid odour, and give also the Prussian-blue and other characteristic hydrocyanic acid tests. Other evidence was also adduced to indicate the formation of hydrocyanic acid in the methæmoglobin solutions when treated with potassium ferri-cyanide; the facts indicate that photomethæmoglobin and cyano-(met)hæmoglobin are identical modifications of the blood-pigment.

S. B. S.

Coaguloses. III. D. LAWROFF (*Zeitsch. physiol. Chem.*, 1908, 56, 343—362. Compare Abstr., 1907, i, 995).—The present experiments were performed with crystallised egg-albumin, and confirm those previously recorded with hæmoglobin and caseinogen. In the various fractions the same two types of coagulose-yielding substances were detected after relatively short peptic digestion.

W. D. H.

General and Physical Chemistry.

Refractive Indices of Gaseous Nitric Oxide, Sulphur Dioxide, and Sulphur Trioxide. CLIVE CUTHBERTSON and E. PARR METCALFE (*Proc. Roy. Soc.*, 1908, A, 80, 406—410).—The refractive index of nitric oxide for sodium light is 1.0002939. This is greater than the value calculated from the indices of nitrogen and oxygen. For sulphur dioxide and trioxide, the values of the index are respectively 1.0006609 and 1.000737. These numbers are much smaller than those calculated from the indices of sulphur and oxygen.

H. M. D.

Refractive Index and Dispersion of Light in Argon and Helium. W. BURTON (*Proc. Roy. Soc.*, 1908, A, 80, 390—405. Compare Scheel and Schmidt, this vol., ii, 333).—The measurements were made by Jamin's interferometer method. The refractive index for the D line at 0° and 760 mm. is for argon 1.0002837; for helium, 1.00003500. The constants A and B in the dispersion equation $n = A + B/\lambda^2$ are for argon 1.0002792 and 1.6×10^{-14} ; for helium, 1.00003478 and 7.5×10^{-16} .

H. M. D.

Dispersion of Gaseous Mercury, Sulphur, Phosphorus, and Helium. CLIVE CUTHBERTSON and E. PARR METCALFE (*Proc. Roy. Soc.*, 1908, A, 80, 411—419. The results obtained for the refractive index and dispersion can be expressed by the formulae: mercury, $\mu - 1 = 0.001755 (1 + 2.265/\lambda^2 \cdot 10^{10})$; sulphur, $\mu - 1 = 0.001046 (1 + 2.125/\lambda^2 \cdot 10^{10})$; phosphorus, $\mu - 1 = 0.001162 (1 + 1.53/\lambda^2 \cdot 10^{10})$; helium, $\mu - 1 = 0.0000347 (1 + 2.4/\lambda^2 \cdot 10^{11})$. The refractive index of sulphur for infinitely long waves is, within 2%, four times that of oxygen; the dispersions also are approximately as 4:1. The index of phosphorus for infinitely long waves is exactly four times that of nitrogen; the dispersions are almost exactly as 2:1. The index of helium is, within 1.6%, one-eighth of that of argon.

H. M. D.

Energetics and Chemistry of Banded Spectra. JOHANNES STARK (*Physikal. Zeitsch.*, 1908, 9, 356—358. Compare this vol., ii, 138).—Polematical against Kauffmann (*Physikal. Zeitsch.*, 1908, 9, 311). The nitro-compounds mentioned by Kauffmann as forming exceptions to the author's view of the dependence of fluorescence on the position of the absorption bands are not suitable substances for the examination of the validity of the theory; absorption bands due to groups other than the nitro-group condition the fluorescence of these substances.

H. M. D.

The Spectra of Oxygen (Doppler Effect with Canal Rays). JOHANNES STARK (*Sitzungsber. K. Akad. Wiss. Berlin*, 1908, 554—577).—The canal rays in oxygen have been examined, and it is found that three of the series lines show the Doppler effect, although only under

specially favourable conditions. The spark lines show the effect the more strongly the greater their intensity. Bands are also conspicuous in the canal ray spectrum of oxygen.

The observations on canal rays in different elements lead to the conclusion that the carriers of the line spectra are the positive ions. It appears also that by the loss of one or more electrons, an atom may give rise to positive ions of different valency. C. H. D.

The Distribution of Intensity in the Spectra of the Canal Rays in Hydrogen. JOHANNES STARK and W. STEUBING (*Sitzungsber. K. Akad. Wiss. Berlin*, 1908, 578—585).—The relation between the distribution of intensity of spectral lines in canal rays and the velocity of the rays has been investigated. With increasing velocity the ratio of the intensity of a line to that of a less refrangible line of the same series increases the more rapidly the smaller the ratio of the wave-lengths of the two lines. C. H. D.

The Resonance Spectra of Sodium Vapour. ROBERT W. WOOD (*Phil. Mag.*, 1908, [vi], 15, 581—601*).—Sodium vapour in an exhausted steel tube, heated to about 400°, shows an extremely complex absorption spectrum consisting of a multitude of very fine absorption lines; the very large scale photographs taken show, for example, about 6000 lines in the bluish-green. If the vapour is illuminated with white light, it becomes fluorescent and gives an emission spectrum which is the exact counterpart of the absorption spectrum. By exciting the vapour with monochromatic light, only a few lines appear in the emission spectrum. These spectra are called "resonance spectra," because they appear to be due to resonance of an electron of the system when monochromatic radiation plays upon it. The principal peculiarities of the resonance spectra are: (1) they always contain a line of the wave-length of the exciting line; (2) they contain one or more series of other lines spaced almost equally; the lines are usually 38 to 39 Ångström units apart. The bluish-green lithium line ($\lambda = 4972$) excites the same series of lines as the barium line 4934. Only light of certain wave-lengths can excite the resonance spectra, for example, the line 5209 is the only one in the spectrum of the silver arc which is active. The electron theory indicates that a non-radiating system of electrons, when disturbed by absorption of radiation of the same frequency as that of one of the electrons, should emit radiations giving a system of equally spaced lines.

Another remarkable spectrum is obtained by exciting the vapour with cathode rays; this is being studied in detail. T. E.

The Long Wave-length Portion of the Barium Spectrum. VICTOR HOELLER (*Zeitsch. wiss. Photographie Photophysik Photochem.*, 1908, 8, 217—234).—The arc spectrum of barium has been photographed between λ 5160 and λ 7090, the first order being employed and compared with the ultra-violet iron spectrum in the second order. A number of new lines are recorded. The bands between λ 5800 and λ 6600 have also been studied, Fabry's formula being found best to express the relations of the oscillation-frequencies. The weak lines in

* *Ann. Physikal. Zeitsch.* 1908, 9, 450—461

the bands are very numerous, and it was found necessary to compute the position of the heads of the bands.

A comparison with the spectra of the alkaline earths leads to the conclusion that the bands in the barium spectrum are due to the metal, and not to the oxide.

C. H. D.

The Spectrum of Iron Observed in the Oxyhydrogen Blow-pipe Flame. GUSTAVE A. HEMSALECH and CHARLES DE WATTEVILLE (*Compt. rend.*, 1908, 146, 962—965).—The method previously described for studying the spectrum of iron in a hydrogen flame (this vol., ii, 336) has been adapted to the study of spectra in the oxyhydrogen flame. Oxygen was passed through a bulb containing iron electrodes between which extremely powerful electric sparks were discharged. The issuing gas was mixed with hydrogen in the burner previously described, and produced a very white and brilliant flame.

Both the visible and the ultra-violet parts of the spectrum were examined, about 200 lines being identified and their relative brightness determined. Some of the ultra-violet lines were obscured by the bands of the water-vapour spectrum.

In the spectrum of iron at the oxyhydrogen flame temperature, there appears to be a concentration of energy between the wave-lengths 3500 and 3900. When air is substituted for oxygen, not only is the general brightness of the spectrum diminished, but the relative intensity of the lines is altered. The lines of the oxyhydrogen flame are those which appear brightest in the arc spectrum of iron, but the relative intensities are different in this case also. The brightest line from the blowpipe flame is 3860.03, whilst the brightest from the arc is 4383.70.

Practically all the lines attributed to iron in the spectrum of the star Sirius have been found in the blowpipe spectrum except the lines of "proto-iron" ("enhanced lines") described by Lockyer.

R. J. C.

Influence of Temperature and Magnetisation on Selective Absorption. HENRI E. J. G. DU BOIS and G. J. ELIAS (*Proc. K. Akad. Wetensch. Amsterdam*, 1908, 10, 839—850).—In continuation of previous work (this vol., ii, 336), the absorption spectra in the visible region of certain solid compounds of chromium, uranium, praseodymium, neodymium, samarium, and erbium have been further examined, mostly at 193°. The effect of magnetisation in resolving and shifting the position of the lines at 193° has been examined, the results for the green, yellowish-green, and red regions of the spectrum of erbium nitrate being given in considerable detail.

G. S.

Application of Optical Properties of Liquids to the Study of Polymerisation and Analogous Phenomena. N. N. ANDRÉEFF (*J. Russ. Phys. Chem. Soc. (Phys.)*, 1908, 40, 191—201).—Substances which, like tartaric acid, exhibit anomalous rotatory dispersion without absorption are regarded as consisting of at least two kinds of molecules having opposite rotatory powers. The author describes a

method by which the number of different kinds of molecules may be determined in this and similar cases.

If q represents any additive property, for example, the rotation of a substance containing molecules of two different kinds, then $Pq = a_1q_1 + a_2q_2$ and $P = a_1 + a_2$, where q_1 and q_2 are the respective values of this property for the two kinds of molecules and P , a_1 , and a_2 denote the total weight and the weights of the different molecules respectively. The values of q_1 and q_2 depend only on the wave-length of the light employed, whilst a_1 and a_2 vary only with external conditions, such as the temperature. Hence at three different temperatures, with which correspond the values a_1' and a_2' , a_1'' and a_2'' , and a_1''' and a_2''' , the three following pairs of equations hold:

- (1) $q' = a_1'q_1/P + a_2'q_2/P$; $a_1' + a_2' = P$;
- (2) $q'' = a_1''q_1/P + a_2''q_2/P$; $a_1'' + a_2'' = P$;
- (3) $q''' = a_1'''q_1/P + a_2'''q_2/P$; $a_1''' + a_2''' = P$.

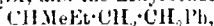
From these, it can be readily calculated that $(q'' - q')/(q''' - q') = (a_1'' - a_1')/(a_1''' - a_1')$, so that $(q'' - q')/(q''' - q')$ is independent of the wave-length. The constancy of this expression for different wave-lengths is hence a criterion for the presence of two kinds of molecules in the substance investigated.

By applying this method to the rotations of tartaric acid, and of dimethyl, diethyl, and dipropyl tartrates for light of various wave-lengths, the author finds that each of the substances contains molecules of two different types.

On the above lines, the author has developed a general theory which leads to a number of determinants, $\delta_1, \delta_2, \delta_3, \dots, \delta_n$; and it is shown that if δ_n is the first of these which has the value zero, the substance contains molecules of n different kinds possessing other than zero values for the optical property considered.

T. H. P.

Relation Between the Rotatory Power of Optically Active Compounds and their Chemical Structure. II. D. A. CHARDIN (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 592—598. Compare Abstr., 1907, ii, 830).—In the present paper is described the investigation of the hexyl alcohol, $\text{CHMeEt}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$, the corresponding bromide, $\text{CHMeEt}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{Br}$, and the hexylbenzene,



on the lines indicated in the previous communication.

From the values of the specific rotation of the hexyl alcohol, the atomic product for oxygen is calculated to be 129.28, the number obtained from a study of active amyl alcohol being 132.32 and the theoretical value 139.4.

Taking the number 211.9 for the atomic product of bromine (*loc. cit.*), the value of $[\alpha]_D^{20}$ for the hexyl bromide is calculated to be $+15.23^\circ$, which deviates from the actual experimental number, $+14.48^\circ$, by about 5%; if, however, the reverse calculation is made from the rotation $+14.48^\circ$, the atomic product for bromine becomes 130.4, which differs from the theoretical value, 211.9, by about 38.5%.

Consideration of the numbers obtained for the hexyl benzene indicates that the linkings of the hydrogen to the carbon atoms in

benzene do not lie in the plane of the ring, but perpendicular to that plane, as suggested by Erlenmeyer, jun. T. H. P.

Anomalous Magnetic Rotation (of the Plane) of Polarisation of the Rare Earths. G. J. ELIAS (*Physikal. Zeitsch.*, 1908, 9, 355).—In reference to Wood's investigation of the anomalous magnetic rotation of neodymium (*Phil. Mag.*, 1908, [vi], 15, 270), the author recalls a similar phenomenon already observed by him in the case of a solution of erbium chloride. H. M. D.

Triboluminescence of Mineral Substances. ADRIEN KARL (*Compt. rend.*, 1908, 146, 1104—1106).—The triboluminescence of many mineral substances is only observed when the eye has become sensitised by a prolonged sojourn in the dark. In other cases, excessive resistance to fracture, or great fragility, has prevented the detection of this property. Triboluminescence is similar to phosphorescence in that it requires the presence of large quantities of a diluent with small quantities of a triboluminogen. Pure substances are not triboluminescent. A triboluminescent system almost always retains the property when subjected to chemical change; thus a triboluminescent manganiferous zinc oxide retains the property when transformed into nitrate or sulphate; the fluoride, however, is inactive.

The study of series of mixtures indicates the existence of an optimum proportion of triboluminogen. These optima are quite different from those of cathodic phosphorescence for the same mixtures. The persistence of triboluminescence in spite of repeated fractionation is very great for some diluents, but purification leads finally to a disappearance of the property.

In the mixtures studied, the diluent was zinc sulphide or oxide, and the triboluminogens, oxides and sulphides of silver, lead, tungsten, tin, bismuth, copper, cadmium, nickel, manganese, uranium, tantalum, niobium, thorium, iron, chromium, zirconium, barium, calcium, vanadium, praseodymium, samarium, dysprosium, magnesium, and silicon. Intimate admixture was effected by simultaneous precipitation or evaporation of the mixed solutions.

The colour of the emitted light varies with the triboluminogen, and is also influenced by the diluent; thus lead gives blue and manganese orange; the system (TiO_2, ZnO) has a pale violet triboluminescence, whilst that of (TiO_2, ZnS) is dark green. The colour is different from that of the phosphorescence of the same mixtures. E. H.

Electrochemistry of Light. II. WILDER D. BANCROFT (*J. Physical Chem.*, 1908, 12, 318—376. Compare this vol., ii, 448).—In the present paper, the mode of action of sensitisers is discussed, the available data being adduced in the form of extracts from the writings of Eder, Vogel, Abney, Timiriazeff, Bothamley, and others. A distinction is drawn between optical sensitisers, which make silver bromide sensitive for certain rays of the spectrum on account of their optical absorption bands, and chemical sensitisers, which are mainly effective by reacting chemically with iodine and bromine.

As to the mode of action of dyes as sensitisers, Abney's view that the dye is oxidised by light is not in accord with the experimental facts, and Eder's suggestion that the dye acts as a catalytic agent is in many respects unsatisfactory. The only theory which accounts satisfactorily for the facts is that of Grotthuss, according to which sensitisers act directly or indirectly as depolarisers. All sensitisers are sensitive to light, and are either reducing agents in the wide sense of the term or are converted into reducing agents by light. The mode of action of cyanin and the eosin dyes as sensitisers is discussed.

There is no connexion between sensitising power and fluorescence.
G. S.

Radioactivity. WILLY MARCKWALD (*Ber.*, 1908, 41, 1524—1561).
—A lecture delivered to the German Chemical Society. G. Y.

Radioactivity. ANDRÉ DEBIERNE (*Bull. Soc. chim.*, 1908, [iv], 3, i—xxxix).—A lecture delivered to the French Chemical Society.
J. C. C.

Law of Transformation in Stages and Radioactivity. GERHARD C. SCHMIDT (*Jahrb. Radioaktiv. Elektronik*, 1908, 5, 115—119).
—The successive formation of disintegration products of the various radioactive substances is supposed to be due to the operation of the general law, according to which the spontaneous transformation of any substance is determined by the least possible diminution of free energy. In consequence of this law, it is improbable that more than one α -particle is emitted in each stage of the disintegration process.
H. M. D.

Radioactivity of Water from Martos and Onteniente. FAUSTINO DIAZ DE RADA (*Anal. Fis. Quim.*, 1908, 6, 290—291).—The following table shows the character of the water from the localities named:

Locality.	Spring.	Temperature.	Initial activity, volts per hour-litre.
Martos	—	20—22°	30.4
Onteniente	El Principal	—	45.8
„	El Pocito	—	74.3

W. A. D.

Radioactivity of Water from Castromonte and Puertollano. JOSÉ MUÑOZ DEL CASTILLO (*Anal. Fis. Quim.*, 1908, 6, 291—292).—The following table shows the character of the different samples of water:

Locality.	Spring.	Temperature.	Initial activity, volts per hour-litre.
Puertollano	Fuente de San Gregorio	16.25°	138.1
„	Los Baños	20°	44.7
Castromonte	—	—	73.5

W. A. D.

Ionisation Phenomena Produced by Snow. G. COSTANZO and C. NEGRO (*Jahrb. Radioaktiv. Elektronik*, 1908, 5, 120—124).—In the expectation that the emanation emitted by the earth's surface would give rise to an abnormally large ionisation of the air contained in layers of fallen snow, the authors have examined such air electroscopically. Whereas the normal fall of potential amounted to 0.2 volt in five minutes, the voltage drop when the air from 25 grams of collected snow was allowed to circulate through the apparatus amounted to 3.5 volts in the same interval. After sixteen hours, when the snow was melted, the fall of potential under the same conditions was 0.5 volt in five minutes. The ordinary air after the snow-fall was found to contain relatively few ions; this is supposed to be due to the ions previously present having acted as centres of condensation.

H. M. D.

Distribution of the Radiation of Radioactive Substances. H. GREINACHER (*Physikal. Zeitsch.*, 1908, 9, 385—392).—The darkening of photographic plates subjected to the action of metallic uranium, which is cut so as to give plane geometrical figures, shows a peculiar distribution. In general, the darkening extends beyond the uranium itself, but at each angle the plate shows a region where the effect is very greatly reduced. The contrast is greater in the case of acute angles than for angles which are obtuse. Experiments are described which show that the phenomenon cannot be attributed to total reflection or to mutual action of the β - and γ -rays resulting in deflexion. Geometrical figures cut from a hardened mixture of uranium oxide and gypsum show the effect described with the same sharpness, and when minium, which readily absorbs β -rays but radiates secondary rays in large quantities, is added to the mixture of uranium oxide and gypsum, very sharply-defined images are obtained. The phenomenon is supposed to be due to secondary rays produced by the β - and γ -rays, and it is shown that the images produced on the photographic plates are displaced under the influence of a strong magnetic field.

H. M. D.

Life of Radium. BERTRAM B. BOLTWOOD (*Amer. J. Sci.*, 1908, [iv], 25, 493—506).—The growth of radium in solutions of ionium has been examined by measuring the emanation contained in the solutions at different times. Five different solutions of ionium were used in the experiments. The first two were obtained from carnotite, the third from Joachimsthal uraninite, the fourth from secondary uranium minerals, chiefly gummite and uranophane, and the fifth from a specimen of very pure uraninite from North Carolina. The amounts of radium produced by the separated ionium in known periods are compared with the quantities of radium originally associated with the quantities of the various minerals operated on, and from these data the disintegration constant of radium is calculated to be 3.48×10^{-4} (year) $^{-1}$. The separate values obtained for the five different solutions are in good agreement, and the half-value period corresponding with this constant is about 2000 years.

H. M. D.

Distribution in Electric Fields of the Active Deposits of Radium, Thorium, and Actinium. SIDNEY RUSS (*Phil. Mag.*, 1908, [vi], 15, 601—614).—A rod charged either positively or negatively to 300 volts is exposed to a definite quantity of the emanation of radium, thorium, or actinium mixed with another gas, and the quantities of active deposit compared when the pressure of the admixed gas is varied. With radium emanation in air, the activity of the negative rod diminishes slowly with the pressure at about 100 mm., but much more rapidly at lower pressures, whilst that of the positive rod increases slightly. The ratio of the activities is about 20 at atmospheric pressure, and about 2.5 at 0.01 mm. In sulphur dioxide the difference of activity is much greater, whilst in hydrogen there is no difference at all up to 1 mm. pressure. With thorium emanation in air, the ratio of the activities of the negative and positive rods is about 200:1 at atmospheric pressure, and about 25:1 at 2 mm., the change being due to a diminution in the activity of the negative rod. With actinium, the ratio is 2:1 at atmospheric pressure, but at 2 mm. pressure it is 22:1, the activity of the negative wire increasing. The ratio in the case of actinium increases, however, as the distance of the electrodes from the actinium becomes smaller. The experiments confirm Rutherford's view that the molecules of the active matter are moving too fast to be directed by the electric field unless they are stopped by numerous collisions with other gas molecules. The experiments with actinium indicate that the sign of their electric charge depends on the distance they have travelled through the gas. T. E.

Determination of the Molecular Weight of Radium Emanation by the Comparison of its Rate of Diffusion with that of Mercury Vapour. P. B. PERKINS (*Amer. J. Sci.*, 1908, [iv], 25, 461—473).—An apparatus is described by means of which the rates of diffusion of mercury vapour and radium emanation have been compared at temperatures of 250° to 275°. The tendency of mercury to oxidise at this temperature made it necessary to carry out the diffusion experiments in an atmosphere of hydrogen. The porous plugs through which the gases diffused were made by boring a large number of cup-shaped holes, 1 mm. in diameter, through an iron tube which divided the apparatus into two chambers; these holes were then filled with fine asbestos fibre. The quantities of diffused emanation were measured by determining the amounts of the induced activity on a negatively charged electrode.

It is pointed out that Graham's law can only be applied with accuracy to the determination of molecular weights when the molecular complexity of the two gases compared is the same, and when the molecular weights do not differ very much from one another. These conditions are fulfilled in the comparative experiments made by the author.

From a number of experiments at 250°, the molecular weight of the emanation is found to be 235; from the experiments at 275°, the calculated value is 234. The author concludes that there can be no

doubt that the molecular weight of the emanation is not very different from that of radium.

H. M. D.

Different Kinds of γ -Rays of Radium and the Secondary γ -Rays which they Produce. R. D. KLEEMAN (*Phil. Mag.*, 1908, [vi], 15, 638—663).—When the γ -rays of radium fall on a substance, secondary γ -rays are given off. It is shown that the primary γ -rays consist of at least three groups of rays. Group *A* is most readily absorbed by lead and mercury, group *B* by zinc, copper, iron, sulphur, and aluminium, and group *C* by carbon. The secondary γ -rays radiated from these substances consist mainly of the two groups which are least absorbed by the substance. The best absorbed group of primary rays produces secondary rays, which are still more readily absorbed, and so do not escape from the substance. The explanation of the phenomena on the hypothesis that γ -rays are pulses in the ether produced by changes in the velocity of corpuscles is discussed.

T. E.

The Range of the α -Rays. WILLIAM DUANE (*Compt. rend.*, 1908, 146, 958—960).—It is well known that the ionising, phosphorescent, and photographic activities of α -rays are completely destroyed when the rays traverse a few centimetres of air or an equivalent thickness of some other substance. Rutherford found that the velocity of the α -rays near the end of their course is reduced to 60% of its initial value. The quantity of positive electricity carried by the α -rays of radium is now shown to be similarly affected by the interposition of air.

The apparatus employed consisted of an electrode contained in a cylindrical brass box which could be evacuated. The α -rays were allowed to enter the end of the box through a window made of extremely thin mica supported on copper gauze. The gauze was insulated from the box and electrode, and connected to a battery, so that the ionising effect of the rays could be measured by the conductivity of the air between the window and the electrode.

For ionisation measurements, a minute quantity of radium chloride was purified from emanation and from induced activity by dissolving in water twice, and was finally dried on a piece of platinum foil. The foil bearing the radium was placed at a known distance from the mica window of the box, and the current carried between the charged gauze and the electrode by the ionised air was measured by a quadrant electrometer. Practically the whole ionisation of the air within the box ceased when the radium was removed 2 cm. from the window. The small ionisation which persists even at longer ranges was attributed to traces of induced activity and emanation remaining in the radium chloride. When the chloride was left for two days so that emanation and induced activity accumulated, it produced considerable ionisation in the box even when 4 cm. from the mica window.

A much larger quantity (almost 0.002 gram) of radium chloride, purified by solution in water as before, was employed to measure the quantity of electricity transported to the electrode by the α -particles.

The box containing the electrode was now evacuated, so that no ionisation current could pass between the window and the electrode, and the charge carried by the α -rays themselves to the electrode was measured with a Wilson electroscope. Secondary radiation towards the electrode was suppressed by placing the apparatus in a strong magnetic field parallel to the electrode. It was found that if the radium was more than 2 centimetres from the mica window, no charge was carried through to the electrode. If the radium was not free from emanation and induced activity, however, the charge could be detected at much greater distances, but could not be attributed to the α -particles.

The charge of the α -particles and their ionising effect are stopped by practically the same thickness of air, namely, 2 centimetres.

R. J. C.

Secondary Rays from the α -Rays. WILLIAM DUANE (*Compt. rend.*, 1908, 146, 1088—1090).—It has been shown previously (preceding abstract) that the charge carried by the α -rays of radium stops at the place where the ionising, photographic, and phosphorescent effects disappear. The experiments now described indicate that the α -rays lose their power of producing secondary rays at the same point. The brass box, containing an electrode and fitted with a mica window, described in the first paper, was again employed. When the radium salt is sufficiently near to the mica window, the α -rays pass through the latter and strike the electrode, producing secondary rays on the surfaces both of the mica and of the electrode. The charge of these secondary rays can be readily measured by evacuating the box and determining the potential of the electrode by means of a Wilson electroscope. If α is the positive charge carried to the electrode per second by the α -rays, s_1 the negative charge removed from the electrode per second by the secondary rays leaving its surface, and s_2 the negative charge carried to the electrode by the secondary rays from the mica window, then the total current i towards the electrode is $i = \alpha + s_1 - s_2$. A large enough magnetic field parallel to the surface of the electrode suppresses s_1 and s_2 , whilst an electric field produced between the mica window and the electrode stops either s_1 or s_2 according to its sense. Thus, in order to determine the current s_1 due to the secondary rays leaving the electrode, it is sufficient to measure, firstly, the current $(\alpha + s_1)$, s_2 being eliminated by an electric field, and, secondly, the current α , s_1 and s_2 being suppressed by a magnetic field.

When the radium is placed 1.4 cm. below the mica window, and the latter is charged at different potentials, the current obtained does not increase after the potential has risen to 85 volts, showing that this is sufficient to stop all the secondary rays s_2 ; moreover, the high potential required for this purpose indicates that the currents are not due to ionisation of the gas remaining in the apparatus.

Radium almost free from emanation and induced activity (as in the former experiments) was placed at different distances below the window, and the currents measured (1) with the window at a potential of +85 volts, and (2) with a magnetic field of 2800 gauss. The difference

of these two currents, representing the charge of the secondary rays, is plotted as a function of the distance of the radium, and the curve obtained shows that the production of secondary rays ceases almost completely when the radium is more than 2 cm. below the mica, that is, the distance at which the other effects of the α -rays disappear.

Similar experiments with polonium gave inconclusive results, owing to the minuteness of the currents produced. E. H.

Method of Counting the Number of α -Particles from Radioactive Matter. ERNEST RUTHERFORD and H. GEIGER (*Mem. Manchester Phil. Soc.*, 1908, 52, No. 9, 1--3).—It should be only just possible with very sensitive apparatus to detect the ionisation of a gas produced by a single α -particle, but by making use of the property of ions moving in a strong electric field in a gas at low pressure of producing a number of fresh ions by collision with the gas molecules, the authors have succeeded in automatically increasing the electrical effect several thousand times and rendering it easily observable. The testing vessel was a long brass tube, along the axis of which a thin insulated wire passed which was connected to the electrometer, the gas pressure being about 2 cm. A potential difference of about 1000 volts between the brass tube and the wire was required. From a film of active matter contained in an exhausted tube, which is a prolongation of the testing vessel, the α -particles were fired through a small hole covered by a mica plate at the rate of from six to ten per minute. The effect of the α -particle entering the testing vessel was shown by a sudden throw of the electrometer needle, and by observing the number of throws it was found that the number of α -particles counted by this method is of the same order as the calculated number. By counting at intervals the number of α -particles expelled per minute, the curves of decay of activity of a plate coated with radium-*C* or actinium-*B* have been obtained. The time interval between the entrance of successive α -particles has been observed over a long interval, and the results show that the distribution curve with time is similar in general shape to the probability curve of distribution of the velocity of molecules in a gas. Further observations are in progress.

J. V. E.

Changes in Velocity in an Electric Field of the α , β , and Secondary Rays from Radioactive Substances. A. S. EVE (*Phil. Mag.*, 1908, [iv], 15, 720—737. Compare Abstr., 1905, ii, 4; H. W. Schmidt, Abstr., 1907, ii, 520).—The author withdraws his previous statement that the secondary rays from substances acted on by the β - and γ -rays of radium are homogeneous. Corrected values for the coefficients of absorption by aluminium of the secondary rays emitted by different substances are given. The experimental data for lead, iron, brick, and carbon indicate that the rays from the lighter substances are more easily absorbed, especially at first. The lighter the substance the less is the secondary radiation, and the smaller the group velocity of the secondary rays the more quickly are these absorbed by the screens. The secondary rays from lead are very similar to the primary radium rays which produce them.

Certain substances, such as brick, slate, wood, paper, and carbon, give rise to very penetrating secondary rays, which originate from layers of the radiator several centimetres deep; these appear to be secondary γ -rays or high velocity negative rays.

It is shown that the velocity of the α , β , and secondary rays can be increased or diminished in a strong electric field the lines of force of which are parallel to the direction of motion of the rays. In the case of the α -particles, there also appears to be a small change in the range of the particles. Experiments on the influence of the electric field on the secondary radiations emitted by different radiators show that these are influenced to varying extents. The changes produced in the group velocity of the secondary rays on reversal of a given field increase as the coefficient of absorption by aluminium increases, and, in consequence, as the density of the radiator diminishes.

These results indicate that the secondary rays are in the main intrinsic, and are emitted with distinctive group velocities depending on the density of the radiator. They are not due to dispersed primary rays, although it is not improbable that a certain fraction of the secondary radiation may consist of such primary rays. H. M. D.

Experimental Investigation of the Nature of γ -Rays. WILLIAM H. BRAGG and J. P. V. Madsen (*Phil. Mag.*, 1908, [iv], 15, 663—675).—An ionisation chamber is closed above by super-imposed plates of different metals (for example, lead and aluminium), the bottom being made of a similar pair of plates. A pencil of γ -rays traverses all four plates, entering at the top. Reversing the top pair of plates makes very little difference in the ionisation in the chamber; reversing the bottom pair, increases it in a very marked way when the lead plate is uppermost. The ionisation is mainly due to secondary radiations from the metal surfaces within the chamber. On the ether pulse theory, the radiation set up by a pulse entering a substance should be the same as that produced on leaving it. The experiment shows that this is not so. The authors propose the hypothesis that γ -rays are unmaterial, and consist of neutral pairs formed from β -rays by taking up a positive charge. The secondary radiation, which is known to contain β -rays, would be produced by the γ -ray losing its positive charge again. The same hypothesis applies to X -rays. T. E.

Electrical Charge of the Active Deposit of Actinium. SIDNEY RUSS (*Phil. Mag.*, 1908, [iv], 15, 737—745).—It has been found that the relative activities of positively and negatively charged plates which are symmetrically exposed to the action of actinium emanation depend on the distance between the actinium and the charged plates, and also on the pressure.

At 760 mm. pressure, the ratio of the activity of the negative to that of the positive plate diminishes as the distance of the plate from the actinium increases; at 2 mm. pressure, the opposite relationship holds good. At the higher pressure, the active matter deposited on the negative plate decreases regularly with increasing distance from the actinium, whereas that deposited on the positive plate

increases at first and then decreases. At the lower pressure, the active matter on the negative plate increases with the removal of the plate from the actinium, whilst that on the positive plate shows a steady decrease.

Experiments with an apparatus which permitted of measurements at longer distances were made at a pressure of 12 mm. It was found in these circumstances that the ratio of the negative to the positive activity first increases and then diminishes.

The author concludes that the electrical charge exhibited by the active deposit particles is mainly determined by the collisions between these particles and the ions or molecules of the gas with which they are in contact.

H. M. D.

Number of Quasi-elastic Bound Electrons in the Helium Atom. H. ERFLE (*Ber. deut. physikal. Ges.*, 1908, 6, 331—338).—From Herrmann's measurements of the dispersion of helium, the author calculates a lower limiting value (p) for the number of quasi-elastic bound electrons in the helium atom. It is shown that there is probably only one type of electron with a vibration frequency corresponding with the ultra-violet region. The corresponding wavelength is $113 \mu\mu$, and the calculated limiting value of the number of the electrons under consideration represents in this case the actual number. Since p is equal to 0.25, it follows that the number of helium atoms in a given volume of the gas is four times as large as the number of quasi-elastic bound electrons in the same volume.

H. M. D.

Meso-thorium. OTTO HAHN (*Physikal. Zeitsch.*, 1908, 9, 392—402).—An account of work, most of which has been already published (compare Abstr., 1907, ii, 359, 664). The changes observed in the activity of commercially-purified thorium preparations, from which meso-thorium is separated by the processes of purification, depend on whether the changes are followed by measurements of the quantity of emanation emitted, or whether the α -rays are examined. The difference is traced to the fact that thorium itself emits α -rays. When the constant α -radiation of thorium is taken into account, the activities of thorium preparations of different ages, measured by both methods, are in good agreement with the activities calculated on the basis of the constants of meso-thorium and radio-thorium.

The α -ray activity of meso-thorium, free from radio-thorium, has been observed during a period of one and a-half years. The observed increase in the activity agrees with that required by the known constants of meso- and radio-thorium. All the later experiments confirm the previous statement that meso-thorium emits β -rays but not α -particles.

H. M. D.

Electrical Conductivity of Alloys and their Temperature Coefficients. W. GUERTLER (*Physikal. Zeitsch.*, 1908, 9, 404—405).—Polemical against Rudolŕi (*Physikal. Zeitsch.*, 1908, 9, 198).

H. M. D.

Aluminium in the Potential Series. CHARLES M. VAN DEVENTER and H. VAN LUMMEL (*Chem. Weekblad*, 1908, 5, 359—363; JOHANNES J. VAN LAAR, *ibid.*, 383, 390).—Polemical (compare van Deventer and van Lummel, this vol., ii, 12; van Laar, this vol., ii, 218).

A. J. W.

Galvanic Self-induction of Metals. CHARLES M. VAN DEVENTER and H. VAN LUMMEL (*Chem. Weekblad*, 1908, 5, 349—356. Compare van Deventer and van Lummel, this vol., ii, 12).—The authors describe experiments with zinc, cadmium, tin, lead, nickel, copper, silver, and platinum in support of their theory of the "leaking insulator."

A. J. W.

Dielectric Constants of Gases at High Pressures. KARL TANGEL (*Ann. Physik*, 1908, [iv], 28, 59—78).—The dielectric constants of hydrogen, nitrogen, and air have been measured at pressures varying from 20 to 100 atmospheres. The values for 20, 40, 60, 80, and 100 atmospheres are for hydrogen at 20°: 1.00500, 1.00936, 1.01460, 1.01926, and 1.02378; for nitrogen at 20°, 1.01086, 1.02135, 1.03299, 1.04406, 1.05498, and for air at 19°, 1.01080, 1.02171, 1.03281, 1.04386, and 1.05494 respectively.

The Clausius-Mossotti formula holds good up to 100 atmospheres; the extrapolated value of the dielectric constant for 1 atmosphere and 0° is equal to the square of the refractive index for infinitely long wave-lengths in the case of all three gases examined.

The dielectric constant of mixtures of hydrogen and nitrogen (D_m) is given by the equation $D_m - 1 = (D_H - 1) + (D_N - 1)$, where D_H and D_N are the dielectric constants for the two gases at the pressures in which they are contained in the mixture. H. M. D.

Reactions in the Iron-Nickel Peroxide Accumulator. II. Behaviour of the Electrolyte. FRITZ FÖRSTER (*Zeitsch. Elektrochem.*, 1908, 14, 285—298. Compare this vol., ii, 146).—The potassium hydroxide solution, which forms the electrolyte in the iron-nickel peroxide accumulator, becomes more concentrated during discharge and vice versa. The change of concentration is almost complete as soon as the charge or discharge is ended; in both cases, the large change is followed by a small gradual increase of concentration, due to decomposition of water by the finely-divided iron of the cathode. The change is therefore due to combination of water with the nickel peroxide electrode during discharge; the quantity taken up is between 1 and 2 molecules for each faraday given out by the cell. The *E.M.F.* of the cell decreases as the concentration of the electrolyte increases; the change is very small (2.8 millivolts when the concentration increases from 2.8*N* to 5.3*N*, for example). A calculation of the change to be expected, based on the vapour pressures of the solutions, gives values of the same order of magnitude as those observed. T. E.

Explanation of Supertension. II. FELIX KAUFER (*Zeitsch. Elektrochem.*, 1908, 14, 321—326. Compare Abstr., 1907, ii, 924).—The resistance of an electrolytic cell with lead electrodes and sulphuric

acid of maximum conductivity as electrolyte is measured during the passage of a current. In these circumstances, there is a "supertension" at the cathode, that is, the apparent fall of potential between cathode and electrolyte is greater than that corresponding with the reversible decomposition of water into oxygen and hydrogen at atmospheric pressure. The addition of a trace of copper sulphate removes this supertension. It is found that the resistance of the cell with copper sulphate is the same as that calculated from the resistance of the sulphuric acid and the dimensions of the cell, but when "supertension" exists it is greater. There is therefore a high resistance film at the surface of the cathode; possibly this is a hydride of lead, the rate of decomposition of which is much accelerated by traces of platinum or copper.

Further experiments are made in the same way as before with a platinised platinum cathode (or anode), which is heated to a higher temperature than the electrolyte by means of a current of electricity. Here there is practically no supertension, and yet reactions (reduction of benzophenone; oxidation of *p*-nitrotoluene) take place at it which usually are observed only at electrodes showing supertension. The author believes that supertension is not the cause, but a symptom, of a reaction. When a finite current is flowing, the electrolytic changes are always irreversible, and the electrode potential, therefore, higher than that corresponding with the main reaction. Traces of substances of higher potential may therefore be formed, and these condition the potential of the electrode.

T. E.

Transport Number for Dilute Hydrochloric Acid. KARL DRUCKER and B. KRĀNJAVI (*Zeitsch. physikal. Chem.*, 1908, 62, 731—742. Compare Jahn, *Abstr.*, 1901, ii, 540; Noyes and Sammet, *Abstr.*, 1903, ii, 126; Noyes and Kato, this vol., ii, 346).—The authors have made a very careful determination of the transport number for chlorine in a solution of hydrochloric acid, special attention being directed to the purity of the materials used and to the accuracy of the analyses. The apparatus employed was essentially that due to Loeb and Nernst, the bulk of solution being large enough to permit the analysis of five sections of the conducting column in addition to the solutions round the electrodes. These were both made of palladium, the anode being charged with hydrogen.

For the transport number of chlorine at 18°, the authors deduce the value 0.1697 from analysis of the anode solution, and 0.1647 from analysis of the cathode solution. The cause of the divergence of these numbers cannot be traced.

Discussion of their own and others' results leads the authors to the conclusion that the transport number for chlorine in highly diluted hydrochloric acid is at least 0.170 at 18°, and that the ionic conductivity of hydrogen at the same temperature is not more than 213.

J. C. F.

Electrochemical Equivalents of Oxygen and Hydrogen. ROBERT A. LEHFELDT (*Phil. Mag.*, 1908, [vi], 15, 614—627).—A form of electrolytic gas voltameter is described wherein the gas is measured

by displacement of mercury, which is weighed. The errors of the measurements of electricity, time, volume of gas, pressure, and temperature are fully discussed; the results are probably correct to less than 1 part in 1000. Solutions of sulphuric acid, sodium hydroxide, sodium sulphate, sodium thiosulphate, disodium hydrogen phosphate, sodium chromate, potassium iodide, potassium dichromate, sodium oxalate, sodium arsenate, sodium nitrate, and sodium chlorate were tried. Of these, sodium sulphate and potassium dichromate give correct results, but the other substances give too little gas; even with sodium hydroxide the quantity of gas obtained varied from 98.5% to 99.8% of the theoretical quantity. The mean of sixteen experiments with sodium sulphate and potassium dichromate was 0.17394 e.e. of gas (under normal conditions) per coulomb, from which it follows that the quantity of electricity required to decompose an equivalent of water (1 faraday) is 96590 coulombs.

T. E.

Amphoteric Electrolytes. BROR HOLMBERG (*Zeitsch. physikal. Chem.*, 1908, 62, 726—730. Compare Bredig, *Zeitsch. Elektrochem.*, 1899, 6, 34; 1904, 10, 245; Walker, *Abstr.*, 1904, ii, 309; 1905, ii, 138; 1906, ii, 735; Lundén, *Abstr.*, 1906, ii, 265, 828; Johnston, *Abstr.*, 1906, ii, 733; Cnmming, *Abstr.*, 1906, ii, 734).—The hydrogen ion concentration in solutions of various amphoteric electrolytes (*o*-, *m*-, and *p*-aminobenzoic acids, *d*-aspartic acid, and *d*-glutamic acid) has been determined by the ethyl diazoacetate catalysis (see Bredig and Fraenkel, *Abstr.*, 1905, ii, 692; Fraenkel, *Abstr.*, 1907, ii, 746). The values so found are in good agreement with the calculated values.

J. C. P.

Electrolytic Valve Action of Zinc, Cadmium, Silver, and Copper. GUNTHER SCHULZE (*Ann. Physik.*, 1908, [iv], 26, 372—392. Compare *Abstr.*, 1907, ii, 842; this vol., ii, 350).—Zinc and cadmium exhibit electrolytic valve action in a solution of potassium carbonate. The normal effect is not obtained in the case of zinc for solutions containing less than 10% of carbonate; at this concentration the maximum voltage is 83V. Cadmium shows the normal valve action in a 1% solution, the maximum voltage for this concentration being 126V. For both metals the maximum voltage decreases rapidly with increasing concentration of the electrolyte. For a given concentration the maximum voltage is much higher for zinc than for cadmium, and this voltage is reached at a much smaller current density in the case of zinc. The diminution of the maximum voltage with rise of temperature is much less rapid for zinc than for cadmium.

Electrolytic valve action is also exhibited by silver in solutions of hydrochloric, hydrobromic, and hydriodic acids, and by copper in a solution of hydrofluoric acid. In these cases the phenomenon appears to be due directly to the formation of a layer of solid on the surface of the anode.

Summarising the results obtained with different metals, the author points out that the faculty of a metal to give rise to electrolytic valve action depends on the particular group of the periodic system to which the metal in question belongs.

H. M. D.

Influence of the Silent Discharge on Explosive Gaseous Mixtures. HEINRICH FASSBENDER (*Zeitsch. physikal. Chem.*, 1908, 62, 743—759).—When a mixture of carbon monoxide and oxygen is exposed to the silent discharge, the rate of explosion is increased. This result, however, is shown to be due to the presence of ozone produced by the discharge. In this connexion, it is noteworthy that when a mixture of carbon monoxide and oxygen is exploded, a piece of potassium iodide-starch paper exposed to the gases is turned blue by the ozone formed in the explosion.

The velocity of explosion of a dry mixture of hydrogen and chlorine is not increased by previous exposure of the mixture in an alternating field. The author's experiments show, however, that during such an exposure the slow combination of hydrogen and chlorine is accelerated. A similar slow combination of carbon monoxide and oxygen is promoted by the influence of an alternating field, but in this case the field must be much more powerful in order to produce the result.

From these experiments it appears that in an explosive gaseous mixture, ionisation and dissociation result from the action of an alternating field, but that this state of dissociation does not persist, the dissociation products combining forthwith to form new neutral molecules. Such a formation of dissociation products and their subsequent combination under the influence of the silent discharge is sometimes so vigorous as to lead to the ignition of the gaseous mixture. This phenomenon was observed especially with mixtures of carbon monoxide and oxygen, a case in which the heat of combination is very great.

J. C. P.

Is the Fixation of Atmospheric Nitrogen in the Electric Discharge to be Regarded as a Purely Thermal Effect? G. BRION (*Zeitsch. Elektrochem.*, 1908, 14, 245—251).—The electric discharge through a gas is carried by a comparatively small number of ions, which have a very much larger kinetic energy than the majority of the molecules. The distribution of energy in the gas is therefore quite different from that in a gas of the same average temperature through which no discharge is passing. The application of the ordinary laws of chemical equilibrium does not, therefore, appear to be justified. The yields of nitric oxide actually obtained in practice are explicable on the assumption of an "electrical" temperature of about 4000° for the molecules which carry the current, but, on the other hand, the small yields obtained with small currents in the glow discharge are not in harmony with this view.

T. E.

Difference of Potential and the Stability of the Alternating Arc between Metals. CHARLES E. GUYE and A. BRON (*Compt. rend.*, 1908, 146, 1090—1093).—The authors find that the difference of potential measured depends within wide limits on the degree of stability of the arc, so that any cause (gas pressure, cooling, air currents, diminution in the self-induction, or the resistance of the circuit, &c.) which tends to diminish this stability, that is, to prolong the duration of the extinction, immediately results in an increase of

the efficacious difference of potential at the electrodes. Similar lack of stability, by producing momentary extinctions, will vitiate experiments with the continuous current arc. By the disposal of a very large reserve tension in the open circuit (20,000 volts) and heating the electrodes almost to their melting point, arcs are obtained of extreme stability. Under these conditions, the extinction period becomes negligible, and the experimental results can be easily interpreted conformably with the views on the mechanism of the arc. The authors show that, other conditions being equal, the potential difference tends towards an inferior limit which is approximately the same for all metals, provided they are only slightly volatile. As the result of experiments in air at 40 cm. pressure for a distance between the electrodes of 4 mm. and an alternating intensity of 0.1 ampere (frequency 50), the limit for platinum, gold, palladium, silver, copper, nickel, iron, and aluminium is found to be approximately 475 volts. For volatile metals the limit is lower.

In the case of long arcs of small intensity between non-volatile metals, the medium between the electrodes (the latter must be incandescent in order to emit the electrons required to maintain the arc), which is ionised by the electrons and which is principally concerned in the difference of potential, is almost wholly air in every case. This accounts for the fact that the potential difference is independent of the nature of the metal. When the ionised medium contains metallic vapours, as in the case of short intense arcs, or with volatile electrode metals, this independence, of course, no longer is observed.

The minimum potential difference obtained as the gas pressure diminishes, already observed with short intense arcs, is also found with the arcs here experimented with. The gas pressure corresponding with this minimum is 5—7 cm.

Thus it seems that below a certain pressure the number of gaseous molecules interposed between the electrodes is insufficient for the normal ionisation, an increase in the potential difference then becoming necessary in order to maintain the same current.

Under the conditions of extreme stability, the law of the decrease of the potential with the pressure is a linear one. . E. H.

Theory of Dulong and Petit's Law. I. FRANZ RICHARZ (*Zeitsch. anorg. Chem.*, 1908, 58, 356—374).—A theoretical paper, which contains a summary of the author's work on this subject published at intervals during the last fifteen years (compare Abstr., 1893, ii, 404). A simple proof is given of the well-known result that the atomic heat of a gas at constant volume is 3. Further, on certain assumptions, based mainly on atomic considerations, it is shown that the atomic heat of solid elements at constant volume is constant and equal to 6.012. The atomic heat at constant pressure is greater, owing to the work done in overcoming the attraction of the atoms, and varies from 6.072 to 6.914 for different elements. The theory also accounts satisfactorily for the fact that some elements have exceptionally low atomic heats (compare Behn, Abstr., 1900, ii, 259).

G. S.

Thermal Expansion and Specific Heat of Metals. E. GRÜNEISEN (*Ann. Physik.*, 1908, [iv], 26, 211—216).—From a comparison of the true coefficients of expansion and the true specific heats of aluminium, iron, nickel, copper, palladium, silver, iridium, and platinum within wide limits of temperature, it is shown that the quotient of the coefficient of expansion by the specific heat is almost independent of the temperature. Except in the case of iridium and platinum, for which the values of the quotient are very nearly constant, the ratio of the two numbers appears to increase slightly with the temperature. For those intervals of temperature in which molecular changes take place, the relationship does not hold. The author supposes that the variations of the expansion and the specific heat with temperature are due to the operation of the same cause, and reference is made to the hypothesis of Richarz relating to the influence of temperature on specific heat.
H. M. D.

Relationship between Compressibilities, Thermal Expansions, Atomic Volumes, and Atomic Heats of the Metals. E. GRÜNEISEN (*Ann. Physik.*, 1908, [iv], 26, 393—402).—The fact that the compressibility of the elements exhibits periodicity has led the author to inquire into the relationship between this and other physical properties for which a similar periodicity has been established. Denoting the compressibility by K , the thermal expansion by α , the volume of a gram atom by v , and the atomic heat at constant pressure by C_p , and applying the kinetic theory to the metals which are supposed to be monatomic in the solid state, it is shown that $3\alpha v/K$ and $3\alpha v/KC_p$ should be constant. For twenty metals, the values of these expressions are shown to be in fairly close agreement; antimony and bismuth show the largest deviations from the mean value. The assumption that the solid metals and liquid mercury are monatomic is in consequence considered to be justified. The relationships involved may be used for the deduction of the compressibilities of metals which have not been subjected to direct measurement. For silicon and liquid chlorine, the expression $3\alpha v/K$ is found to have the same value as it has for metals.
H. M. D.

Change of Density and Specific Heat of Platinum and Nickel after Treatment, and the Dependence of the Specific Heat on the Temperature. WILHELM SCHLETT (*Ann. Physik.*, 1908, [iv], 26, 201—210).—The changes which take place in the density and specific heat of platinum and nickel after various kinds of mechanical treatment, such as hammering, rolling, and cold-drawing, and also after heating to a high temperature, have been examined. In both cases the more dense form of the metal has the smaller specific heat, a relationship already pointed out for the allotropic modifications of the non-metals. From a comparison of the variations of the specific heat with the temperature and with the density, the conclusion is drawn that a rise of temperature causes molecular changes to take place which are very different from those brought about by mechanical treatment.

The true specific heat of nickel between 0° and 300° is given by

$C_t = 0.10280 + 0.0000941t$, and that of platinum by $C_t = 0.030456 + 0.00002972t + 0.000000561t^2$.

H. M. D.

Practice of Oryometric Measurements. PODA (*Zeitsch. angew. Chem.*, 1908, 21, 1066—1069).—A freezing-point apparatus is described by means of which accurate determinations can be carried out rapidly. The vessel in which the liquid is contained consists of a double-walled tube expanded to form a bulb in the lower half; by means of a tube sealed on to the bulb, the space between the two walls communicates with a levelling tube through a piece of thick-walled rubber tubing. By raising or lowering the levelling tube, the space between the walls of the freezing vessel can be filled with mercury or exhausted; by this means ice which has separated out from an aqueous solution can be quickly melted, or during a measurement the loss of heat by radiation can be reduced to a small value. A simple form of stirrer is also described, and numbers are recorded for the freezing points of sucrose and potassium chloride solutions.

H. M. D.

Stand for Apparatus for Cryoscopic Measurements. ROBERT LESPIEAU (*Bull. Soc. chim.*, 1908, [iv], 3, 613—617).—A stand is described provided with (1) a small platform on which the refrigerator vessel and its contents can be placed, (2) a driving-wheel by which the thermometer suitably provided with a pulley can be caused to rotate in the solution under examination, and (3) a support in which the thermometer rotates. The stand is figured in the original.

T. A. H.

Calculation of Thermochemical Constants. H. STANLEY REDGROVE (*Chem. News*, 1908, 97, 253—255, 266—268. Compare Abstr., 1907, ii, 604; this vol., ii, 463).—The molecular heats of combustion and molecular heats of formation of eight ethers, nine primary, one secondary, and two tertiary alcohols, three aldehydes, two ketones, nine esters, three organic acids, and one organic anhydride have been calculated by means of the author's system of "fundamental constants." For thirty-four substances out of the thirty-eight up to the present considered, the results are in excellent agreement with those values actually found by Thompson. A table of the "Fundamental Molecular Heat of Combustion and Formation, Oxygen Constants" is also given.

J. V. E.

New Method for Determining Vapour Densities. III. PHILIP BLACKMAN (*Ber.*, 1908, 41, 1588—1591; 2487—2488. Compare Abstr., 1907, ii, 931; this vol., ii, 137).—A small error in the author's method of determining vapour densities, caused by air bubbles trapped in the mercury column, is overcome by heating the mercury and re-reading the gas volume after the temperature has again reached that of the laboratory. Details are quoted of vapour density determinations with a number of substances to illustrate the accuracy of the method.

G. Y.

Application of a Deduction from the Boyle-Mariotte Law. H. REBENSTORFF (*Chem. Zeit.*, 1908, 32, 570).—From the equation for isothermal alteration of a closed volume of a gas, the expression $\Delta v/v' = \Delta p/p$, as also $\Delta v/v = \Delta p/p'$, has been arrived at; this is called the "alteration law," and states that the alteration of volume is to the one volume as the alteration of pressure is to the other pressure. Use is made of this relationship for finding the volume of large air vessels in a rapid and convenient manner. The vessel the capacity of which is to be measured is connected by a rubber tube carrying a pinch clip to a graduated glass tube filled with water, and covered at its lower end with a piece of fine muslin. On opening the pinch clip, water flows out of the tube, giving a measure on the scale of the alteration of volume Δv of the unknown volume v , and at the same time a measure of the decrease of pressure Δp from the original atmospheric pressure p' . From this, the unknown volume of the vessel may be calculated from the equation above. By lowering a weighted bottle, the mouth of which is covered by muslin, into water and measuring the water that has been forced into the bottle by the increased pressure, an approximate estimation of the depth of the water may be obtained.

J. V. E.

Molecular Aggregations Produced in Gases by Sudden Cooling. GWILYM OWEN and A. LL. HUGHES (*Phil. Mag.*, 1908, [vi], 15, 746—761. Compare Abstr., 1907, ii, 843).—The previous experiments on the production of condensation nuclei by cooling gases to low temperatures have been extended. It is now found that the effect depends to a large extent on the rapidity of the cooling process. By cooling rapidly, condensation nuclei are formed in air at temperatures considerably higher than the maximum temperature in the case of slow cooling. At a given temperature below this maximum, the number of nuclei produced is much greater when the air is cooled very quickly than when slow cooling takes place. The so-called "nucleating temperature" also varies with the size of the apparatus into which the gas to be cooled is admitted, but this phenomenon is supposed to be simply due to a difference in the rate of cooling which is attainable when cooling vessels of different sizes are employed.

Carbon dioxide can be cooled to its condensation temperature without nuclei being produced; when the condensed solid sublimes, large nuclei are, however, formed. Ethylene does not show a "nucleating temperature," but with methane results are obtained similar to those met with in the case of air. The phenomena in mixtures of those gases can be accounted for when the partial pressures of the components are taken into consideration.

Experiments made to determine the influence of temperature on the persistency of the nuclei show that rise of temperature increases the rate of disappearance. The nuclei are not electrically charged.

H. M. D.

Osmotic Pressure. ISIDOR TRAUBE (*Pflüger's Archiv*, 1908, 123, 419—432).—The direction of osmosis is determined by the difference of surface tension towards air of the liquids separated by the membrane. This difference is termed the "surface pressure," and is regarded,

instead of the osmotic pressure, as the directing force governing osmosis. The membrane also plays some part in the process, for, according to Willard Gibbs, substances which lower the surface tension of a solvent have a tendency to collect on the surface. The dissolved substance also has an influence on the solvent, exerting what is termed a cohesion pressure; the more a substance lowers the surface tension of a solvent the smaller is this cohesion pressure.

The smaller the cohesion pressure exerted by a substance the more readily will it tend to be eliminated from the solution, and the more readily will it be dissolved or adsorbed by a second liquid or solid phase in contact with the solution.

A simple relationship can be deduced between the lowering of surface tension, adsorption, and the coefficient distribution of a substance between two solvents.

In the above theory, the cohesion pressure of a substance in the separating membrane will also exert influence on the rate and direction of diosmosis.

This theory, too, which takes into account the cohesion pressure, is capable of explaining facts which are not explicable by Overton's theory of the distribution of substances between lipoids and non-lipoids, as, for example, the absorption of peptones which are not readily soluble in lipoids.

It has been applied to explain this, and other absorption phenomena in the digestive tract, and also the action of the kidneys, where it can be shown that there is an intimate relationship between the functional capacity and the surface tension of the urine. The theory has also been applied to explain the action of lymphagogues and certain phenomena of parthogenesis, also hemolysis, narcosis of the ganglia, plasmolysis, &c.

S. B. S.

Relation between the Diffusion Constant, Internal Friction, and Electrical Conductivity. LEO PISSARJEWSKY and E. KARP (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 599—611*).—After discussing the work of Jones and Lindsay (Abstr., 1903, ii, 55), Jones and Carroll (Abstr., 1905, ii, 73), Pissarjewsky and Lemcke (Abstr., 1905, ii, 684), and Walden (Abstr., 1906, ii, 335), the authors give the results of their own determinations of the diffusion constant, internal friction, and electrical conductivity of solutions of sucrose, sodium chloride, sodium hydroxide, ammonia, and acetic acid in water or aqueous alcohol.

When the diffusing substance is a non-electrolyte, such as sucrose, the product of the diffusion constant and the internal friction, $D\eta$, is a constant, and for acetic acid this product also remains comparatively constant.

In the case of electrolytes, the values of $D\eta$ vary as much as 30%. If this variation depends on differences in the degree of dissociation, the value of $D\eta/\alpha$ should exhibit greater constancy than $D\eta$. It is first shown that $D\eta/\alpha = D\mu_r/\mu'_r$, where μ_r and μ'_r are the molecular conductivities of the substance in water and the given solvent respectively, and then found by conductivity measurements of aqueous

* and *Zeitsch. physikal. Chem.*, 1908, 63, 257—268.

and aqueous alcoholic *N*-sodium chloride and of 4/7*N* solutions of sodium chloride in water and sucrose solutions that $D\mu_0/\mu'_0$ is constant.

It also seems probable that for all electrolytes in all solvents, $D\eta\sqrt{M}/a$ is constant. When D and η are given, this relation renders it possible to calculate a , and then, having determined μ_0 and η_0 , to calculate μ_∞ for the given electrolyte in the given solvent according to the formula $a = \mu_0\eta_0/\mu_\infty\eta_\infty$.

When the dilution is such that a has the value unity, the above relations become $D\eta = \text{constant}$ and $D\eta\sqrt{M} = \text{constant}$, and as, also, $\mu_\infty\eta$ is constant, we have $D/D' = \mu_\infty/\mu'_\infty$, that is, the ratio of the diffusion constant of any given electrolyte to its molecular conductivity at infinite dilution is constant for different solvents.

T. H. P.

Time Taken by Substances in Dissolving. GASTON GAILLARD (*Compt. rend.*, 1908, 146, 1020--1022. Compare Abstr., 1908, ii, 241).—In the experiments described, given weights of various substances (sodium thiosulphate, sodium sulphate, sucrose) were introduced into fixed quantities of solvent at a known temperature and agitated by a turbine-driven stirrer regulated to a constant known velocity, and the time elapsing between the addition and the total disappearance of the substance observed. Only the results of experiments in which portions of the same sample of substance and the same rate of stirring were employed can be compared, since the size of the crystals and the rapidity of diffusion have considerable influence on the time of dissolution. The following results are obtained: (1) With increasing quantities of the same substance, the ratio of the time to the concentration obtained is (within the limits of the experiments) at first practically constant, and then increases. (2) In certain cases the curve, obtained by plotting reciprocals of the times against the corresponding temperatures, is comparable with the solubility curve. But salts of equal solubility may take widely different times to dissolve, and the variation of the time with the temperature does not always follow that of the solubility. (3) For some mixtures of salts (potassium chromate and sulphate, ammonium and potassium nitrates, sodium chloride and potassium nitrate) the variation in the time is in the same sense as the modification in the solubility, but these variations are small. (4) A table is given showing the increase in the times required for the dissolution of successive equal quantities of sodium chloride or sucrose in the same quantity of solvent, each addition being made immediately after the disappearance of the preceding quantity of substance.

E. H.

Influence of Temperature on Complex Formation in Solution. ALFRED BENKATH (*Zeitsch. anorg. Chem.*, 1908, 58, 257—264. Compare Abstr., 1907, ii, 694).—From the results of ebullioscopic, and in some cases of cryoscopic, determinations with mixtures of two salts in water and in alcohol as solvents, it is shown that when there are deviations from additive behaviour, they are greater at the freezing point than at the boiling point. This is best accounted for on the

view that complexes of the two salts partly decompose as the temperature is raised.

Cobalt and cupric chlorides do not appear to combine with sodium chloride in aqueous solution at 100° even when the concentration of the latter salt is high, but in alcoholic solution the elevation of the boiling point for mixtures of lithium chloride with cobalt and cupric chlorides respectively is smaller than the sum of the effects due to the salts separately. Mixtures of nitrates which give an abnormally small freezing-point depression behave normally at the boiling point. Cadmium chloride does not combine appreciably with sodium chloride at the boiling point of the aqueous solution. Experiments have also been made with mixtures of mercuric chloride and potassium and sodium chlorides respectively.

G. S.

Influences of Solubility. GIUSEPPE KERNOT, E. D'AGOSTINO, and M. PELLEGRINO (*Gazzetta*, 1908, 38, i, 532—554).—The authors have studied the influence of increasing proportions of (1) potassium chloride on the solubility of calcium hydroxide, (2) ammonium chloride on the solubility of barium carbonate, and vice versa. The results, which are given in the form of both tables and curves, are briefly as follows.

In presence of increasing quantities of potassium chloride, the solubility of calcium hydroxide at first increases and afterwards diminishes, becoming less than the solubility in water alone (compare Rothmund, *Abstr.*, 1900, ii, 467; Rothmund and Wilsmore, *Abstr.*, 1902, ii, 447; Hoffmann and Langbeck, *Abstr.*, 1905, ii, 374).

The solubility of barium carbonate rises continuously as the amount of ammonium chloride present increases, and at 25°, when the solution contains about 5 mols. of the chloride, the solubility curve assumes an upward inflexion, which is probably due to the formation of a double chloride of barium and ammonium. The relation of the solubility of ammonium chloride to the proportion of barium carbonate present is represented by a curve perfectly analogous to the preceding one.

Conductivity curves indicate that the degree of dissociation of potassium chloride is not altered by the presence of calcium hydroxide, or that of ammonium chloride by the presence of barium carbonate. The conductivity of the mixed solution may be regarded as the sum of the conductivity of the saturated solution of the substance influenced and that of the solution of the influencing substance, so that the amount of the substance influenced which is brought into solution or expelled therefrom by the influencing substance does not participate in the formation or destruction of the electric molecules.

In order to obviate difficulties in the analysis of the mixed solutions, the authors have made use of the following method, which reduces all the determinations to simple weighings. The two substances are weighed, one after the other, into the same vessel, which is placed in a thermostat in which it can be rotated. Water is then gradually added to the vessel, avoiding contact with the air, until the two substances are completely dissolved. This may be effected con-

veniently by means of two flasks, one inverted above the other, the two being connected by means of a glass tube passing through rubber stoppers in the two flasks and having its lower end drawn out to a fine point. The upper flask is filled to the extent of about 19/20 with water, which may be forced into the lower flask in quantities as small as desired by gently warming the air in the upper flask.

T. H. P.

Solubilities in Mixed Solvents. WALTER HERZ and F. KUHN (*Zeitsch. anorg. Chem.*, 1908, 58, 159—167. Compare Abstr., 1904, ii, 709; 1905, ii, 510, 709; 1907, ii, 159, 848).—The solubility of mercuric chloride, bromide, iodide, and cyanide in mixtures of methyl and ethyl alcohol in varying proportions has been determined at 25°, and the density and viscosity of the solutions have also been determined.

For the bromide, iodide, and cyanide, $L-l$ (L =observed solubility, l =solubility calculated on the assumption that the components exert their effect independently) is small, and may be positive or negative. The solubilities and densities increase, and the viscosities decrease, throughout as the proportion of methyl alcohol increases. For mercuric chloride, $L-l$ is fairly large for intermediate concentrations, and is positive throughout; the different behaviour in this case is probably to be ascribed to the fact that the salt combines with methyl alcohol (McIntosh, Abstr., 1897, ii, 372). For the chloride, bromide, and cyanide, $L-l$ attains its maximum value for the mixture containing the components in equivalent proportions.

G. S.

[Vapour Pressure of Dry and of Ordinary Sal Ammoniac.] JOHANNES J. VAN LAAR (*Zeitsch. physikal. Chem.*, 1908, 62, 678—680. Compare this vol., ii, 353).—A further criticism of Abegg's views (this vol., ii, 157, 466).

J. C. P.

Thermodynamics of the Sulphuryl Chloride Equilibrium $\text{SO}_2 + \text{Cl}_2 = \text{SO}_2\text{Cl}_2$. MAX TRAUTZ, E. BAISCH, and ALFRED VON DECHEND (*Zeitsch. Elektrochem.*, 1908, 14, 271—280).—In order to calculate the equilibrium between sulphuryl chloride, sulphur dioxide, and chlorine, it is necessary to know the vapour-pressure curve of sulphuryl chloride, its heat of evaporation, and the specific heat of the vapour. Details of the methods used in determining these quantities are given. The results obtained are: vapour pressure (in mm. of mercury) at -78° , 0.2 ; 0° , 40.92 ; 17.99° , 95.2 ; 34.73° , 209.6 ; 40.13° , 263.9 ; 45.26° , 322.1 ; 50.42° , 392.1 ; 55.25° , 467.8 ; 60.09° , 555.9 ; 64.94° , 656.2 ; 69.62° , 766.9 . Many other points on the curve were determined. The heat of evaporation (per molecule) at pressure p and absolute temperature T is given by $\lambda = (1 - p/55)(8940 + 3.5T - 0.02845T^2)$. The molecular heat of the vapour at 43 mm. pressure between 16° and 99° is 15.5 .

T. E.

Equilibrium Between Metals and Solutions of Metallic Salts. EMIL BOSE (*Zeitsch. Elektrochem.*, 1908, 14, 314—316).—By means of the apparatus already used for silver and gold (Abstr.,

1907, ii, 735; this vol., ii, 264), it is now shown that platinum is more soluble in a hot concentrated solution of platinum tetrachloride than in a cold one. The difference is very small, and prolonged circulation is required in order to obtain a precipitate of platinum in the cold tube. The equilibrium is $\text{Pt} + \text{Pt}^{4+} \rightleftharpoons 2\text{Pt}^{2+}$. A bibliography of investigations dealing with equilibria of this kind is given. T. E.

Influence of the Solvent on the Equilibrium Constant. LEO PISSARJEWSKY and A. LEVITES (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 611—623).—The influence of the solvent on the equilibrium constant is often very considerable. Thus, K of the reaction $\text{CaSO}_4 + 2\text{OH}' \rightleftharpoons \text{SO}_4^{''} + \text{Ca}(\text{OH})_2$ in 10.5% aqueous mannitol solution is eleven times, and in 23.7% aqueous glycerol solution nineteen times, as small as in water, whilst K of the reaction $\text{Ag}' + \text{Fe}'' \rightleftharpoons \text{Fe}^{'''} + (\Delta\text{g})$ in 10.5% mannitol solution is about sixteen times as small as in water. Comparison of the changes of free energy in the reaction $\text{CaSO}_4 + 2\text{OH}' \rightleftharpoons \text{SO}_4^{''} + \text{Ca}(\text{OH})_2$ in water and in equal molecular aqueous solutions of methyl and ethyl alcohols, ethylene glycol, glycerol, and erythritol leads to the empirical relation $A = A_0 - 100B\eta$, where A and A_0 are the changes of free energy in the alcoholic solution and water respectively, B the number of hydroxyl groups in the alcohol employed, and η the relative internal friction of the alcoholic solution. In all cases where the degrees of dissociation of the reacting substances in the various solvents are identical, it seems probable that the product $A\eta$ is a constant. By the gradual addition of glycerol to water, the change of the free energy of the reaction $\text{CaSO}_4 + 2\text{OH}' \rightleftharpoons \text{SO}_4^{''} + \text{Ca}(\text{OH})_2$ diminishes in such a manner that the product of the free energy into the number of mols. of added glycerol is constant. The marked influence of the solvent on the equilibrium constant may also be applied to the determination of the change of free energy of non-reversible reactions. T. H. P.

Transition Concentrations. I. Conversion of Lanthanum Oxalate into Sulphate by Sulphuric Acid. F. WIRTH (*Zeitsch. anorg. Chem.*, 1908, 58, 213—227).—The equilibrium in the condensed system lanthanum oxalate and sulphate and the free acids has been investigated in the usual way by solubility measurements at 25°, and the relations are discussed on the basis of the phase rule.

The solubility of oxalic acid in water diminishes on progressive addition of sulphuric acid, at first rapidly, and then, beyond 12% of acid, comparatively slowly. The solubility of lanthanum oxalate in water increases with the concentration of sulphuric acid up to 1.9 mols. of the latter in 1000 grams of solution, at which point the solution contains 0.0264 mol. of lanthanum oxide in 1000 grams. As the concentration of sulphuric acid is further increased, the lanthanum oxalate is gradually converted into sulphate along the "transition curve," the proportion of lanthanum oxide in solution at the same time steadily decreasing. The transition curve oxalate \rightarrow sulphate meets the two solubility curves of lanthanum oxalate and sulphate respectively in sulphuric acid in the presence of solid oxalic acid at a triple point at which the solution is in equilibrium with the

three solid phases. At this point, the solution contains about 2.5 mols. of sulphuric acid and 0.011 mol. of lanthanum oxide in 1000 grams. The solid salts in equilibrium with the solution at the triple point are $\text{La}_2(\text{C}_2\text{O}_4)_3 \cdot 7\text{H}_2\text{O}$ and $\text{La}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$. G. S.

Equilibria in Quaternary Systems. FRANZ A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1908, 10, 817—823).—The equilibria in certain quaternary systems have been investigated by solubility measurements in the usual way, and the results are represented on projected space diagrams.

The systems water, methyl and ethyl alcohols and ammonium nitrate; water, methyl and ethyl alcohols and potassium nitrate, and water, ethyl alcohol, ammonium and silver nitrates, have been investigated at 30°. The latter system is the most complicated, as a double salt, $\text{NH}_4\text{NO}_3 \cdot \text{AgNO}_3$, exists, which is soluble without decomposition in water and in 71% alcohol, but is decomposed by 91% alcohol. Equilibria similar to the last named occur at 30° in the systems water, ethyl alcohol, silver nitrate and potassium nitrate, and water, alcohol, benzoic acid and ammonium benzoate; in the latter case, a double compound of benzoic acid and ammonium benzoate is formed.

The equilibria in the system water, ethyl alcohol, ammonium and manganese sulphates are very different at 50° and 25°; at the former temperature, an anhydrous double salt, $2(\text{MnSO}_4)_2 \cdot (\text{NH}_4)_2\text{SO}_4$, and the hydrate, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, are stable, and at the latter temperature the compound $\text{MnSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$. G. S.

Reactions in Solutions of Different Salts, but with the Same Ions. ALBERT J. J. VANDEVELDE (*Chem. Zentr.*, 1908, i, 1360; from *Rev. gén. Chimie*, 1908, 11, 57—59).—It has been shown previously (*Abstr.*, 1907, ii, 609) that the velocity of reaction is not influenced by the substitution of copper for zinc in copper sulphate solution, but depends on the nature of the ions present; Cl ions increase and SO_4 ions retard the reaction. The production of the copper solution is effected equally well from $\text{CuSO}_4 + \text{NaCl}$ or $\text{CuCl}_2 + \text{Na}_2\text{SO}_4$; the same applies to acid solutions, for example, $\text{H}_2\text{SO}_4 + 2\text{NaCl}$ and $2\text{HCl} + \text{Na}_2\text{SO}_4$, &c. J. V. E.

Estimation of the Concentration of Hydrogen Ions by Indicators. LEONOR MICHAELIS and PETER RONA (*Zeitsch. Elektrochem.*, 1908, 14, 251—253).—A simple way of estimating the concentration of the hydrogen ions in a solution (between 0.0005 and 0.01*N*) is to add Congo-red to the solution, and compare this colorimetrically with a solution containing a known quantity of hydrochloric acid. The authors find, however, that the colour is changed by neutral salts, the acidity apparently decreasing. Salts of the alkali metals have the same effect, those of bivalent metals a greater effect, and those of trivalent metals a still greater one. Measurements of the *E.M.F.* of concentration cells with hydrogen electrodes show that no change occurs in the concentration of the hydrogen ions. The change of colour is the first stage in the precipitation of the colouring matter, and is analogous to the change of colour of a colloidal solution

of gold which precedes coagulation. Methyl-violet behaves in a similar way, the change of colour being, however, in the opposite direction. Phenolphthalein and methyl-orange also exhibit colour changes when very large quantities of neutral salts are used.

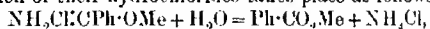
T. E.

Kinetics of the Sulphonation Reaction. HAARVARD MARTINSEN (*Zeitsch. physikal. Chem.*, 1908, 62, 713—725. Compare Abstr., 1905, ii, 149; 1907, ii, 609).—The author has studied the rate at which *p*-nitrotoluene undergoes sulphonation when dissolved in sulphuric acid. The possibility of following the course of the reaction depends on the fact that *p*-nitrotoluene is nitrated with great rapidity by nitric acid, whereas this reagent has no appreciable effect on *p*-nitrotoluenesulphonic acid. A determination therefore of the quantity of nitric acid used up by a given volume of the reaction mixture serves to indicate the extent to which sulphonation has proceeded at any selected time. As in the earlier work (*loc. cit.*), the nitrometer was employed in the determination of unused nitric acid.

One of the reagents, namely, the sulphuric acid, was always present in large excess, and it was therefore expected that sulphonation would proceed according to the formula for a unimolecular reaction. This is borne out generally by the experimental results, which, however, bear evidence also to the marked influence of traces of water, even the small amount produced in the reaction leading to a decrease of the velocity-coefficient as time goes on. Three solvent media were used, namely: (1) absolute sulphuric acid containing 2.4% SO_3 ; (2) absolute sulphuric acid; (3) an acid containing 99.40% H_2SO_4 and 0.49% H_2SO_3 . The values of the velocity-coefficient observed in these three media were respectively 0.003, 0.0004, and 0.0000005. The temperature-coefficient of the velocity is 2.0—2.5 for a rise of 10° .

J. C. P.

Catalysis. V. Catalysis of Imino-esters. WILLIAM McCracken (*Amer. Chem. J.*, 1908, 39, 586—613. Compare Derby, this vol., i, 419).—Stieglitz (this vol., ii, 167, 168) has given an account of the catalysis of imino-esters, and has stated that the decomposition of their hydrochlorides takes place as follows:



and that it proceeds most rapidly with the salts of those imino-esters which are the weakest bases.

An investigation of this decomposition has now been carried out with the object of ascertaining whether it is the salt or the free base which undergoes the change into ester and ammonia, and also of determining whether there is any general relation between the velocity of decomposition of the salts and the affinity constants of the bases. The velocity of reaction and the hydrolysis constants have been determined with the hydrochlorides of ethyl, *isobutyl*, and *isopentyl* iminobenzoates, ethyl imino-*p*-toluate, methyl imino-*o*-toluate, ethyl iminophenylacetate, ethyl imino-*m*-nitrobenzoate, ethyl imino-*m*-bromobenzoate, and ethyl imino- β -naphthoate.

The results show that the velocity of decomposition of these imino-

esters by water is proportional to the concentration of the salt formed with the acid, that is, of the positive ester ions. The whole salt does not undergo decomposition, but only its positive ions. The presence of an excess of hydrochloric acid decreases the velocity of reaction by reducing the degree of ionisation of the imino-ester salt, thus diminishing the active mass of the positive ester ions, and simultaneously tends to increase the velocity by a "salt effect." The acceleration due to the "salt effect" is practically the same for the same excess of acid acting on the salts of two imino-esters, of which the velocities of decomposition are as 10:1. This fact confirms the view that the "salt effect" is not due to a primary action on the salt, but to an effect on the active mass of water involved in the reaction. With two exceptions, the velocity constants were found to decrease as the strength of the imino-esters as bases increased. E. G.

Artificial Peroxydiastases. JULES WOLFF (*Compt. rend.*, 1908, 146, 1217—1220. Compare this vol., i, 490).—The oxidation of pyrogallol under the combined influence of hydrogen peroxide and a colloidal solution of iron ferrocyanide has been studied in detail. The colloidal ferrocyanide solution used contained 0.0023 mg. of iron per drop, and the hydrogen peroxide solution 7mg. of active oxygen per drop. The total volume of solution in each experiment was 40 c.c., and the amount of pyrogallol present was 1.2 grams.

With a constant quantity of hydrogen peroxide (eight drops) and increasing quantities of ferrocyanide, the yield of purpurogallin is proportional to the amount of peroxydiastase until the latter reaches ten drops, after which the amount of purpurogallin increases more and more slowly.

In the presence of a fixed amount of ferrocyanide, the quantity of purpurogallin formed rises regularly as the amount of hydrogen peroxide present increases to nine drops, after which the increase in yield becomes less and less.

In experiments in which twenty drops of ferrocyanide solution and five drops of hydrogen peroxide solution were used, addition of 2.5 mg. and 5.0 mg. of sulphuric acid reduced the yield of purpurogallin 17% and 62% respectively, whilst 0.85 mg. of ferrous sulphate or 0.89 mg. of copper sulphate produced a 70% reduction, but 0.84 mg. of manganese sulphate had very little effect. A similar prejudicial action of ferrous sulphate has been observed by Stoecklin (*Thesis*, Geneva, 1907) in the case of the natural peroxydiastase.

Amongst salts, potassium dihydrogen phosphate has a markedly noxious effect. •

The conclusion is drawn that this colloidal ferrocyanide acts in all its essential respects like a natural enzyme. E. H.

[Deduction of the Stoichiometric Laws.] EMIL BAUR (*Zeitsch. physikal. Chem.*, 1908, 62, 760—761).—A reply to de Vries (this vol., ii, 366). J. C. P.

Commensurability of Atomic Weights. GUSTAVE D. HENRICHES (*Compt. rend.*, 1908, 146, 971—973).—In a previous paper (*Abstr.*, 1907, ii, 945), it was assumed that a perpendicular from the origin of

co-ordinates upon the graph of the equation of condition in a given determination of atomic weight was equal to the deviation of the atomic weight from the "absolute" (round number) value. This is now said to be true only if the values of the analytical excess "e" in the equations of condition are distributed about the origin conformably with the laws of probability. Otherwise, a more detailed discussion of the experimental errors is necessary in order to determine the deviation of an atomic weight from the round number.

The atomic weight of silver is calculated from the synthesis of silver nitrate to be $(108 - \frac{1}{2}) = 107.875$. Hydrogen is calculated to be $16/(16 - \frac{1}{8}) = 1.00787$, whilst chlorine is given as $(35.5 - \frac{1}{2} \times \frac{1}{2}) = 35.458$.

The author claims that his results lend support to the hypothesis of the unity of matter, but the differences between successive elements must be expressed in terms of a smaller unit than hitherto.

R. J. C.

Atomic Weights of Sixteen Chemical Elements. GUSTAVE D. HINRICHS (*Chem. Zentr.*, 1908, i, 1240; from *Mon. Sci.*, 1908, [iv], 22, i, 155-172).—From the published data, the author has calculated the atomic weights of the following elements by the method previously suggested (*Abstr.*, 1893, ii, 317): bismuth, lead, mercury, iron, tellurium, potassium, bromine, iodine, manganese, cadmium, cobalt, indium, platinum, didymium, terbium, and radium. The difference of the calculated atomic weights from whole numbers is found to be decreased and often is due to experimental error. The probability of these values being whole numbers is raised to 10^{14} : 1 for the 28 elements up to the present considered.

J. V. E.

Non-Metallic Elements in Connexion with Valency and Specific Gravity. GEORGE WOODLISS (*Chem. News*, 1908, 97, 265. Compare this vol., ii, 368).—From a consideration of the relationship existing between the valency and specific gravity and specific gravity and atomic weight of the non-metallic elements immediately preceding in Mendelëff's table the elements of the argon group, evidence is advanced for the valency of these inert elements being 0.5 and not zero. When the quotients of specific gravity divided by the square root of the assumed valency (0.5) of the elements argon, krypton, and xenon are plotted against their atomic weights, it is found that they are in close agreement with other non-metallic elements.

J. V. E.

Valency on an Atomistic Electrical Basis. JOHANNES STARK (*Jahrb. Radioaktiv. Elektronik.*, 1908, 5, 121-153).—A theoretical paper, part of which has been published previously (compare this vol., ii, 138). An attempt is made to account for chemical action by assuming that the atoms consist of positively charged spheres on the interior surface of which are the relatively minute negative electrons. The forces which operate in the union of two different atoms are entirely of electrical nature, and combination takes place as the result of the partial displacement of the lines of force of such a superficial negative electron (termed a valency electron) from the positive sphere

of the atom to which it originally belonged to the positive sphere or spheres of neighbouring atoms. Three kinds of electrons, depending on the way in which the lines of force from the electron are related to the positive spheres of neighbouring atoms, are distinguished. These are classified as unsaturated, saturated, and displaced electrons. On the basis of these three types, the various kinds of dissociation which give rise to the phenomenon of electrical conductivity are explained. The banded spectra of compounds are discussed in reference to the properties of the saturated and the displaced electrons. The line spectra are supposed to be due to internal electrons and not to the valency electrons. Finally, an interpretation of the variation of the valency of the elements along the vertical groups and horizontal series of the periodic table is given.

H. M. D.

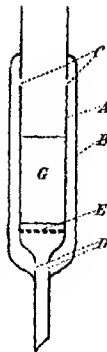
Steam Distillation under Reduced Pressure. WILHELM STEINKOFF (*Chem. Zeit.*, 1908, 43, 517).—The author suggests the use of this method for separating a substance volatile in steam which is itself decomposed by it, or a substance volatile in steam from substances decomposed at the ordinary temperature by such treatment. Toluene is found to distil with steam at $27.5^{\circ}/27$ mm., aniline at $33^{\circ}/20$ mm., nitrobenzene at $22.5^{\circ}/19$ mm., and a 40% yield of benzoyl chloride is obtained at $21^{\circ}/16$ –17 mm.

J. V. E.

Receiver for Vacuum Distillation. GUSTAV KOLBE (*Chem. Zeit.*, 1908, 32, 487).—A modification of Lothar Meyer's apparatus (*Abstr.*, 1887, 884), the valve plug being made of glass rod instead of glass tubing; the exhaust tube is placed in such a position that none of the distillate can be drawn up into it. By means of a special device, it is possible to exhaust the receiver independently of the rest of the apparatus.

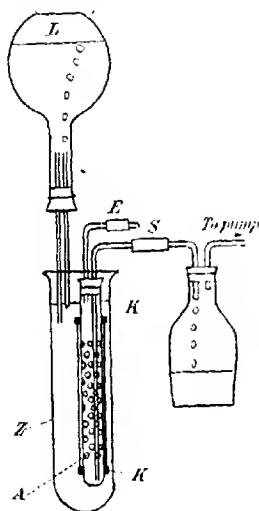
P. H.

Apparatus for Simultaneously Extracting a Solid and Filtering the Solution So Obtained. FREDERICK RECORD (*Chem. News*, 1908, 97, 280).—An apparatus devised to obviate the loss of substance which occurs in the course of filtration subsequent to the extraction of solids with such solvents as ether and alcohol. It consists of an inner tube, *A*, sealed to a shorter concentric jacket, *B*, and in that portion of *A* which is within *B* there are two pairs of holes, *C* and *D*. The substance to be extracted, *G*, is placed above a filter disk, *E*, and covered with filter paper and asbestos. A reflux condenser is attached to the upper part of the apparatus, and a flask containing the solvent to the lower end. The vapour from the boiling solvent rises through apertures *D* and *C* into the condenser, from which the liquid drops upon the substance to be extracted, and percolates through again.



to the flask
J. V. E.

Filter for Filtering Solutions of Definite Concentration at a Temperature Either Above or Below that of the Surrounding Medium. A. LEVITES (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 623—624).—The author has devised a filtering apparatus which may be employed with advantage in cases where the change of concentration occurring when an open filter is employed is to be avoided. Over one end of a glass tube, 4 cm. long and having an internal diameter of about 6 mm., three or four glass fibres, about $\frac{1}{3}$ mm. thick, are soldered parallel to one another so as to form a kind of grating. Over this grating is placed a filter paper, which also extends some distance along the tube, and is kept in position by a piece of rubber tubing, the latter serving also to connect the glass tube with a similar shorter piece. The pipette containing the liquid to be filtered may be connected with the filtering apparatus by means of rubber tubing. Suction may be employed to hasten the filtration. T. H. P.



Filtration Apparatus. HANS WISLIZENUS (*Chem. Zentr.*, 1908, i, 1238; from *Zeitsch. Chem. Appar.*, 3, 89—93).—The inner tube *A* is of porcelain or glass, and is perforated by a number of small holes. Over this is wound a broad strip of moistened filter paper, which is kept in position by two indiarubber bands *KK*. A double bored indiarubber stopper fitting into the mouth of *A* carries two tubes, one of which, *S*, is a suction tube and extends to the bottom of *A*; the other, *E*, reaches only just below the stopper, and is closed during the process of filtration by means of a glass plug on the outside. For ordinary use with cold solutions, the part of the apparatus described is supported in a wide cylinder, *Z*; but when filtra-

tion is required to be carried out at a higher or a lower temperature, the cylinder *Z*, containing the tube *A*, is placed in a heating or cooling bath. The liquid in *Z* to be filtered is best maintained at a constant level by the arrangement indicated by *L*. This apparatus has been found most useful when dealing with slimy or colloidal extracts. J. V. E.

Inorganic Chemistry.

Condition of Steam. EMIL BOSE (*Zeitsch. Elektrochem.*, 1908, 14, 269—271).—The high density of steam is most readily explained by assuming it to contain single and double molecules in equilibrium, $(\text{H}_2\text{O})_2 \rightleftharpoons 2\text{H}_2\text{O}$. The density (air=1) should then be $\Delta = \delta - K/p(\sqrt{1 + \delta p/K} - 1)$, where δ is 1.2432, the theoretical density for $(\text{H}_2\text{O})_2$, p is the pressure, and K is the equilibrium constant at any temperature T . Using determinations of the density made by Kornatz (*Diss.*, Königsberg, 1908), the author calculates $\log K = -4857.1/T + 2145.5$. The values of the density calculated by these equations show a mean deviation from the experimental results of 0.4%. Regnault showed that the deviations of the vapour density of steam from the theoretical value are a function of the degree of saturation of the steam, that is, of the ratio p/P , where P is the pressure of saturated steam, whereas the author represents them as a function of p/K . It is shown that P is approximately proportional to K , so that formally either ratio may be used.

T. E.

Atomic Weight of Chlorine. E. C. EDGAR (*Mem. Manchester Phil. Soc.*, 1908, 52, No. 7, 1—2).—The method used to redetermine this constant was to burn pure dry chlorine at the tip of a quartz jet in an atmosphere of pure dry hydrogen in a quartz combustion vessel, the hydrogen chloride formed being condensed in a limb of it by means of liquid air.

The mean of eight determinations gave the atomic weight of chlorine, calculated from the ratio weight of chlorine burnt/weight of hydrogen burnt, to be 35.194, and from the ratio weight of hydrogen chloride caught/weight of hydrogen burnt, to be 35.193 (at. wt. of hydrogen=1). If the atomic weight of oxygen is taken as 16, that of chlorine becomes 35.462 and 35.461 respectively, numbers which differ appreciably from that accepted by the International Committee on Atomic Weights, but in close agreement with 35.463 found by Dixon and Edgar and 35.461 found by Guye.

J. V. E.

Study of the Oxidation Phenomena Produced by Iodic and Bromic Acids. HENRI BAUBIGNY (*Compt. rend.*, 1908, 146, 1097—1100 *).—An ammoniacal solution of silver chloride or bromide when heated at 100° with iodic acid, contrary to the statements in certain text-books, does not give any deposit of silver iodide. The latter is only formed when the temperature has been raised to 200°, and in this case a slight excess pressure in the cooled tube indicates the evolution of a small quantity of gas.

and *Bull. Soc. chim.*, 1908, [iv], 3, 767—771.

When 45 c.c. of ammonia (D 0.926) are heated with 1.1 grams of iodic acid in a sealed tube at 210° for five hours, a small amount of gas is evolved and an appreciable quantity of ammonium iodide formed. At 150° very little iodide is produced. In three experiments similar to the above, to each of which 0.256 gram of silver bromide was added, 0.0006 gram of silver iodide was formed at 100° , 0.0021 gram at 150° , and 0.1760 gram at 210° .

The conclusion is drawn that the iodic acid oxidises the ammonia, $\text{NH}_4\text{IO}_3 + 2\text{NH}_3 = \text{NH}_4\text{I} + 3\text{H}_2\text{O} + \text{N}_2$, giving water, nitrogen, and ammonium iodide, of which the latter reacts with silver bromide, giving the less soluble silver iodide.

Entirely similar results are obtained with bromic acid, which is not completely destroyed in the experiment, showing that it has a certain stability under these conditions. Since therefore no bromic acid could be detected in the mother liquors of the three experiments described above, it is concluded that none is formed (contrary to the assertions of text-books). Similarly, with silver chloride at 210° , no chloric acid is produced.

E. H.

Origin of Atmospheric Ozone, and Causes of the Variation of Carbon Dioxide in the Air. H. HENRIET and BOISSY (*Compt. rend.*, 1908, 146, 977—978).—A preliminary note, in which the authors summarise the conclusions drawn from a series of experiments on the origin of atmospheric ozone, and the causes of the variation of carbon dioxide in the air. Ozone is formed at the expense of the oxygen of the high regions of the atmosphere under the influence of the ultra-violet rays of the sun; it is carried to the lower layers of the air by winds and rain; the proportion of ozone in the air is at a maximum during a West or South-west wind and at a minimum during an East wind, and it is also increased during clear, calm weather by the direct action of the solar radiations on the lower layers of air. The amount of carbon dioxide in the air varies inversely with that of the ozone for values below the normal; for values above the normal, the variation of carbon dioxide is due to local phenomena, such as fog, animal respirations, combustions, &c.

M. A. W.

Vapour Pressure of Sulphur at Low Temperatures. OTTO RUFF and HUGO GRAF (*Zeitsch. anorg. Chem.*, 1908, 58, 209—212).—The authors' results for the vapour pressure of sulphur at low temperatures (Abstr., 1907, ii, 947) are considerably higher than those given by Gruener (Abstr., 1907, ii, 869); this is ascribed to the inaccuracy of the method employed by the latter observer. Some fresh determinations at 0° and 49.7° have been made by the method previously used, with the slight modification that a second condensing tube, cooled to -185° , was employed. Hydrogen was used as indifferent gas. The results previously given have to be corrected by adding the vapour pressure of sulphur at 0° 0.0013 mm. Results are given for temperatures between 49.7° and 211.3° . At 49.7° , 131.9° , and 211.3° , the corrected pressures are 0.00034, 0.081, and 3.14 mm. respectively.

G. S.

Hydrogen Persulphides. I. Historical. Crude Hydrogen Persulphide. IGNAZ BLOCH and FRITZ HÖHN (*Ber.*, 1908, 41, 1961—1971).—The authors give a historical account of the polysulphides of hydrogen from their discovery in 1777. By heating sodium sulphide with varying amounts of sulphur in an atmosphere of hydrogen for three hours on the water-bath and dissolving the products in water, the authors obtain solutes of the composition Na_2S_3 , Na_2S_4 , Na_2S_5 , and Na_2S_6 . When the solutions are allowed to flow into mixtures of equal parts of ice and hydrochloric acid (D 1.19) cooled in a freezing mixture, crude hydrogen persulphide is obtained as a yellow, oily liquid with the odour of sulphur chloride and camphor. It is decomposed instantaneously by alkalis, and therefore it is essential that all apparatus used in the preparation should be washed with an acid. The oil can be kept for an hour without visible decomposition. Water decomposes it, but dilute acids, particularly hydrochloric acid, act as preservatives. A criterion of purity is the fact that the freshly-prepared persulphide yields a clear solution in benzene. Alcohols, ether, ethyl acetate, and acetone decompose the oil more or less rapidly, whilst with aldehydes and ketones condensation occurs, yielding substances rich in sulphur. Estimations of the hydrogen and sulphur alone do not suffice to fix the composition of the persulphide, but from the amount of hydrogen sulphide liberated by heating, the authors prove the incorrectness of Rebs' statement (*Abstr.*, 1888, 1155) that the hydrogen persulphide obtained by the decomposition of polysulphides by acids always has the composition H_2S_3 . C. S.

Hydrogen Persulphides. II. Hydrogen Trisulphide. IGNAZ BLOCH and FRITZ HÖHN (*Ber.*, 1908, 41, 1971—1975).—Crude hydrogen persulphide (preceding abstract) is distilled under reduced pressure. In order to prevent the deposition of sulphur during the distillation, it is necessary to pass dry hydrogen chloride through the apparatus before it is evacuated. The fraction passing over at 69°/2 mm. is collected in three portions, and the middle one analysed. The estimations and the molecular weight in benzene by the cryoscopic method point to the composition H_2S_3 .

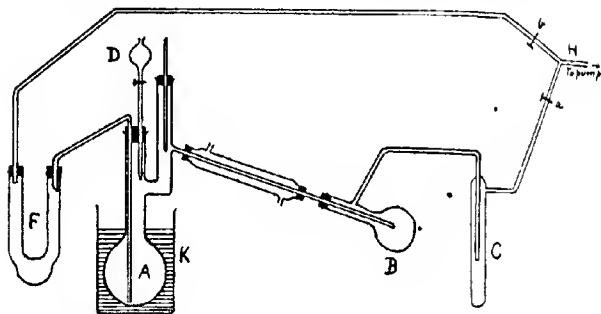
Hydrogen trisulphide, H_2S_3 , m. p. -52° to -53° , D^{25}_4 1.496, is a pale yellow oil, which becomes colourless at lower temperatures. It decomposes slowly in the dark, more quickly in daylight, and rapidly on warming, evolving hydrogen sulphide and depositing rhombic sulphur. It is decomposed slowly by acids, and rapidly by alkalis or alcohols; its solution in ether, benzene, or carbon disulphide is relatively stable. C. S.

Hydrogen Persulphides. III. Hydrogen Disulphide. IGNAZ BLOCH and FRITZ HÖHN (*Ber.*, 1908, 41, 1975—1980).—By means of the apparatus described later, crude hydrogen persulphide has been separated into hydrogen trisulphide and *hydrogen disulphide*, H_2S_2 , b. p. $74-75^\circ$, D^{20}_4 1.376, which resembles the trisulphide in many respects, but differs from it in its greater volatility, greater sensitivity to alkalis, and in the more aggressive character of its vapour. It does not solidify in an ether-carbon dioxide mixture.

The apparatus figured has been designed for the distillation under

reduced pressure of large quantities of a liquid in small portions at a time, the residue being removed after the distillation of each portion without disconnecting the apparatus. Its use in the separation of hydrogen di- and tri-sulphides is as follows.

The flask *A*, of 300 c.c. capacity, immersed in the glycerol bath *K*, is connected through the condenser with *B* (150 c.c.), which is attached to the strongly-cooled vessel *C*. By means of a tube reaching to the bottom, *A* is connected with the U-tube *F*. Between *H* and the water-pump are vessels containing soda-lime and calcium chloride, and a manometer. The flask *A* can be connected with the pump either through *B* and *C* by means of the stopcock *a*, or through *F* by the



stopcock *b*. To carry out the distillation, the bath *K* is raised to 110–125°, and the apparatus evacuated to about 20 mm., *a* being open and *b* closed. From the dropping funnel *D*, about 15 c.c. of crude hydrogen persulphide is run slowly into *A*. Distillation commences; when it becomes irregular, *a* is closed and *b* opened, whereby the residue in *A* is drawn over into *F*. The distillation is then continued by closing *b*, opening *a*, and introducing another 15 c.c. of hydrogen persulphide into *A* from *D*. The liquid collecting in *B* is mainly hydrogen trisulphide, whilst the more volatile disulphide is found in *C*.
C. S.

Hydrogen Persulphides. IV. Constitution of Hydrogen Disulphide and Trisulphide, and the Chemistry of Sulphur Compounds. IGNAZ BLOCH (*Ber.*, 1908, 41, 1980–1985).—The relationships of hydrogen di- and tri-sulphides (preceding abstracts) with one another and with other compounds of sulphur are discussed. The author points out that the change of colour of the two sulphides with change of temperature is perhaps explicable by an intramolecular change, $\text{H}_2\text{S}_2\text{S} \rightleftharpoons \text{HSiSH}$, analogous to keto-enol tautomerism,
 $\text{H}_2\text{C}:\text{C}:\text{O} \rightleftharpoons \text{HC}:\text{C}:\text{OH}$.

Mendeléeff's conception of a homologous series of hydrogen sulphides, H_2S_n , derived from hydrogen sulphide itself by the successive replacement of H by SH receives favourable consideration.
C. S.

Existence of Compounds of Sulphur and Iodine. FRITZ EPFRAIM (*Zeitsch. anorg. Chem.*, 1908, 58, 338—352. Compare Smith and Carson, this vol., ii, 32).—The freezing-point curve of mixtures of sulphur and iodine has been determined, and the results indicate that the elements do not enter into chemical combination and only form one series of mixed crystals, containing 7—8% of sulphur. Further, boiling-point determinations with the two elements in carbon disulphide afford no evidence of combination in that solvent. The two compounds described by Schneider (Abstr., 1888, 414) as double compounds of iodides of sulphur with arsenic trisulphide and the compound SnSI_2 , respectively do not exist; the former is a mixture of arsenic trisulphide and iodine and the latter of stannic iodide and sulphur.

G. S.

Sulphuric Acid Contact Process. LOTHAR WÖHLER, W. PLÜDDERMANN, and P. WÖHLER (*Zeitsch. physikal. Chem.*, 1908, 62, 641—677. Compare Wöhler, Foss, and Plüddemann, Abstr., 1906, ii, 846; Wöhler, Plüddemann, and Wöhler, this vol., ii, 290).—The efficiency of any agent in promoting the union of sulphur dioxide and oxygen is measured by the amount of change which it induces under given conditions, such change being expressed as a percentage of the change which would be observed if the system reached its equilibrium position. Numerous experiments have been made in which chromium oxide, copper oxide, cupric and cuprous chromites, aluminium oxide, ferric oxide, thorium, cerium, silicon and titanium dioxides were used as catalytic agents at temperatures up to 900°. In all these cases, it is found that the efficiency, measured in the way already defined, increases regularly as the temperature rises without any sign of a maximum so long as the condition of the catalytic surface is unchanged. The experiments reveal the very marked influence which sintering has in diminishing the efficiency of the catalytic surface, and occasionally observed cases of a temperature of maximum efficiency are shown to be due to this cause.

It appears probable that the relative adsorptive power of variously treated samples of a given catalyst can be taken as a measure of the relative catalytic efficiency of these samples, but there is no such relation between the adsorptive power and the catalytic efficiency of different catalysts.

The authors conclude that the action of catalysts in the sulphuric acid contact process can be equally well explained by supposing the intermediate formation of a solid solution, either of a gas or of a chemical compound, in the surface layer.

In a note added to the paper, the authors discuss the discrepancies between their results (this vol., ii, 290) and those of Képpeler and D'Ans (this vol., ii, 289).

J. C. P.

Action of Metals on Aqueous Solutions of the Persulphates. MARIO G. LEVI, E. MIGLIORINI, and G. ERCOLINI (*Gazzetta*, 1908, 38, i, 583—602. Compare Abstr., 1907, ii, 81).—After discussing the work of Bringhenti (*Atti R. Ist. Veneto*, 1905, 64, ii, 1321) and Turrentine (this vol., ii, 104), the authors give the results of a study of the action of a large number of metals on solutions of potassium and ammonium persulphates.

All the metals examined, except gold and platinum, react with persulphate solutions, either passing directly into solution or remaining undissolved in the form of oxides or basic salts. In general, the reaction is slower for ammonium than for potassium persulphate, probably owing to the slightly greater degree of dissociation of the potassium salt; in the catalysis with platinum, the tendency is in the opposite direction.

A special case is presented by magnesium, which reacts with extreme violence with ammonium persulphate, causing evolution of ammonia.

In general, those metals go into solution as anions which in their general chemical behaviour exhibit a marked non-metallic character, such as chromium, manganese, selenium, arsenic, molybdenum, &c.; some metals of this type, however, such as antimony, are transformed into insoluble oxides. The general action with these metals is hence oxidation by the persulphate with intervention of water.

Elements which are distinctly metallic in character pass into solution as cations, the persulphate being decomposed, sometimes with evolution of gas. With zinc, nickel, cobalt, &c., no gas is evolved, and in these cases the reaction is probably represented by $\text{Zn} + \text{X}_2\text{S}_2\text{O}_8 = \text{ZnSO}_4 + \text{X}_2\text{SO}_4$, or by (1) $\text{Zn} + \text{X}_2\text{S}_2\text{O}_8 + \text{H}_2\text{O} = \text{ZnO} + \text{H}_2\text{SO}_4 + \text{X}_2\text{SO}_4$ and (2) $\text{ZnO} + \text{H}_2\text{SO}_4 = \text{ZnSO}_4 + \text{H}_2\text{O}$; according to the latter interpretation, the solution may remain neutral or become acid, this depending on the relative velocities of the reactions (1) and (2). When gas is evolved, this is found to be hydrogen, at any rate for concentrated persulphate solutions.

The reactions studied are, except in the cases of gold and platinum, more chemical than catalytic in nature. They proceed with different velocities for different metals, although the velocity does not always bear any evident relation to the oxidisability of the metal or to its readiness of attack by sulphuric acid. The tendency to form double salts or complexes doubtless plays a part.

T. H. P.

Contact Oxidation of Ammonia and Organic Bases. E. I. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 659—660).—When ammonia is oxidised by the author's contact process (this vol., i, 306), it undergoes transformation mainly according to the equation $4\text{NH}_3 + 3\text{O}_2 = 2\text{N}_2 + 6\text{H}_2\text{O}$, a small quantity of the nitrogen being also found as nitrous and nitric acids.

Organic bases, such as aniline, toluidine, and pyridine can also be oxidised in this way.

T. H. P.

Reduction of Hydroxylamine at Copper Cathodes. JULIUS TAFEL (*Chem. Zeit.*, 1908, 32, 135—136).—In reply to Patten (*ibid.*, 44), the author reasserts that hydroxylamine is not reduced at a copper cathode under the conditions expressly stated in his paper (Abstr., 1902, ii, 559). His current researches in conjunction with Hahl (this vol., ii, 175) show that reduction occurs only when the concentration of the sulphuric acid round the cathode falls below a certain value.

C. S.

Electrolytic Reduction of Hydroxylamine. VICTOR ROTHMUND and O. FLASCHNER (*Zeitsch. anorg. Chem.*, 1908, 58, 183—188. Compare Flaschner, *Abstr.*, 1907, ii, 454).—Remarks on Tafel and Hahl's recent paper (this vol., ii, 174). The authors maintain that the use of a stirring arrangement is of great advantage in such investigations.

G. S.

Action of Ammonia on Phosphorus. Observations on the Modifications of Phosphorus. ALFRED STOCK and OTTO JOHANNSEN (*Ber.*, 1908, 41, 1593—1607).—The paper opens with a résumé of the work of various authors on the action of ammonia on phosphorus. As conflicting statements have been made, the question has been re-studied. The present experiments were performed with a specially purified colourless phosphorus, which was freed from traces of arsenic by distillation in a current of steam. The results described show that when colourless phosphorus is treated with liquid ammonia, it is converted more or less completely, depending on the temperature and time of action, into red phosphorus. At the same time, small amounts of a solid hydride and an amide, or imide, of phosphorus are formed; the acid hydride combines with ammonia to form a black salt, which colours the whole mass. When treated with an acid, the red or yellow hydride is liberated, and, on addition of ammonia, again forms the black salt. The amide, when heated, is converted into phosphorus nitride, P_3N_5 .

The red phosphorus, prepared by the action of ammonia on the colourless modification, is identical with Schenck's phosphorus (*Abstr.*, 1904, ii, 117); both have D^{22} 2.02, and are soluble in hot dilute sodium hydroxide. Ordinary red phosphorus, D^{22} 2.17, and Hittorf's phosphorus, D^{22} 2.35—2.37, are insoluble in sodium hydroxide. Both forms of red phosphorus have m. p. 600—615°; Hittorf's phosphorus, m. p. 620—625°; colourless phosphorus, when heated, changes into the red modification, and melts above 600°. All four modifications when heated in sealed tubes form a yellow liquid, which, on cooling, commences to deposit red crystals at about 550°. The relations of the four modifications of phosphorus to each other are discussed.

G. Y.

Action of Ammonia on Phosphorus Chloronitride. ADOLPHE BESSON and ROSSET (*Compt. rend.*, 1908, 146, 1149—1151. Compare Stokes, *Abstr.*, 1895, ii, 217).—By acting on phosphorus chloronitride with liquid ammonia, a white compound, PN_3H_4 , is formed according to the equation $PNCl_2 + 4NH_3 = 2NH_4Cl + PN(NH_2)_2$. This substance is very soluble in water, and, when heated at 220° for several days, loses ammonia and yields phospham, $PN(NH_2)_2 = NH_3 + PN_2H_3$. When dry gaseous ammonia is passed into a solution of phosphorus chloronitride in dry carbon tetrachloride, slender, silky, prismatic needles are obtained having the composition $P_2N_3H_2Cl_2$, and formed according to the equation $2PNCl_2 + 2NH_3 = NH_4Cl + P_2N_3Cl_2 \cdot NH_3$. The compound is insoluble in ether or carbon disulphide, but dissolves in water with slow decomposition. The carbon tetrachloride drained from the crude product probably contains a mixture of ammonium

chloride and the compound PN_3H_4 . The action of gaseous ammonia on phosphorus chloronitride may therefore be represented as follows: $3\text{PNCl}_2 + 6\text{NH}_3 = \text{P}_3\text{N}_3\text{Cl}_3 \cdot \text{NH}_3 + 3\text{NH}_4\text{Cl} + \text{PN}(\text{NH}_2)_2$. The chloro-derivative is regarded as an intermediate product, and the compound PN_3H_4 as being formed by using an excess of ammonia. J. C. C.

Polymeric Forms of Metallic Arsenic. HUGO ERDMANN and RUDOLF REPPERT (*Annalen*, 1908, 361, 1—31. Compare Abstr., 1903, ii, 73, 74).—It is found that the transformation of solid, yellow arsenic, As_4 , into metallic arsenic, As , under the influence of light takes place in two stages, grey arsenic, which is considered to have the constitution $\text{As}:\text{As}$, being formed intermediately. The brown modification, D^{30} 3.67—3.69, formed by the action of light on dissolved yellow arsenic, must have the constitution $\begin{smallmatrix} \text{As}:\text{As}:\text{As}:\text{As} \\ | \\ \text{As}:\text{As}:\text{As}:\text{As} \end{smallmatrix}$. This is formed also

when dissolved yellow arsenic is treated with oxygen, arsenious bromide, or acetylene tetrabromide, or is allowed to remain in the dark.

An improved apparatus is described and figured for the preparation of a carbon disulphide solution of yellow arsenic. This modification, As_4 , D^{50} 2.35, D^{18} 2.026, is unstable in violet or ultra-violet light, but is converted into metallic arsenic only slowly when exposed to red light; radium rays are without effect on the rate of this change.

Grey arsenic, As_2 , D^{20} 4.64, is formed as a by-product in the preparation of the carbon disulphide solution of the yellow polymeride, and is obtained also when the solid yellow arsenic is exposed to light at low temperatures or dissolved yellow arsenic is treated with alcohol or cooled with carbon dioxide and ether or with liquid air. It is stable towards atmospheric oxygen, and is oxidised by nitric acid more slowly than the brown modification or metallic arsenic.

The yellow, grey, and brown polymerides of metallic arsenic do not conduct electricity, whereas metallic arsenic is a conductor. This difference is employed to determine the temperature at which metallic arsenic is formed from its polymerides at a sensible rate. It is found that, when heated, brown arsenic changes into the grey modification, which decomposes into metallic arsenic at about 303° .

When solutions of yellow arsenic and silver nitrate are mixed together, the arsenic, if present in excess, reduces the salt quantitatively to metallic silver, but, if the silver nitrate is in excess, the arsenic is precipitated in the metallic state. Yellow arsenic also precipitates mercury from solutions of mercurous nitrate, and from copper sulphate, a black substance containing 53% to 55% of copper and considerable amounts of arsenic and sulphuric acids. Yellow arsenic therefore is a strong reducing agent, resembling yellow phosphorus, which gives similar reactions. Although isomorphous and chemically closely related, yellow phosphorus and yellow arsenic do not form mixed crystals; this is ascribed to the marked differences in the solubilities. G. Y.

Compounds of Arsenic and Antimony Pentafluoride with Nitrosyl Fluoride. OTTO RUFF [with KURT STAUBER and HUGO GRAF (*Zeitsch. anorg. Chem.*, 1908, 58, 325—337. Compare Abstr., 1906, ii, 20).—The compound $\text{AsF}_5 \cdot \text{NOF}$ is obtained pure by passing

nitrosyl fluoride, NOF (prepared in the same operation by passing nitrosyl chloride through a platinum tube containing dry silver fluoride and heated to 250–280°), through cooled arsenic trichloride until absorption is complete, the product being finally kept over fused sodium hydroxide in a vacuum for some time to absorb traces of nitrosyl chloride. The compound forms a white, crystalline mass, and is remarkably stable; it is unaffected in dry air even at a high temperature, but decomposes in moist air; it is split up by water, by alkali, and by concentrated hydrochloric acid, but is unacted on by phosphorus trichloride, carbon tetrachloride, silicon, copper, lead, and other substances. On warming gently with antimony pentafluoride, arsenic pentafluoride and the solid antimony compound described below are obtained.

The corresponding antimony compound, SbF_5NOF , is obtained in an analogous way by the action of nitrosyl fluoride on antimony pentafluoride, but more simply by interaction of nitrosyl fluoride and a solid antimony chlorofluoride, $(\text{SbF}_6)_3\text{SbCl}_2$. (The latter compound is obtained by the action of chlorine on antimony trifluoride, and will be described later.) The chlorofluoride and nitrosyl chloride are mixed in a tube at -80° , and the mixture allowed to warm up; the tube is then sealed, and kept for one to two hours at room temperature with occasional shaking. The compound occurs in slender, colourless needles, which sublime without decomposition below a red heat; it is very hygroscopic, and is decomposed by water and by alcohol. On warming with arsenic trifluoride, it gives arsenic pentafluoride mixed with excess of the trifluoride, and, on heating with potassium fluoride, it yields nitrosyl fluoride and a compound of antimony pentafluoride and potassium fluoride.

G. S.

Absorptive Power for Air of Certain Varieties of Vegetable Carbon. ARNALDO PIUTTI and G. MAGLI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1908, [iii], 14, 68–75).—The density and absorptive power for air of different forms of carbon are tabulated in the original. The absorption was carried out at the temperature of liquid air, and the air absorbed driven off by heating the carbon gradually to a temperature of 550°.

The maximum absorption is shown by the carbon of cherry-stones and coconut-shell (about 280 and 250 times the volume respectively); this absorption is increased nearly 20 per cent. by a preliminary treatment of the material with chlorine. With the exception of that from arab seed, the surface of which is not sufficiently porous, the absorptive power of charcoal from any material is nearly proportional to its density.

W. A. D.

Solutions of the Alkali Metals in Liquid Ammonia. OTTO JOFFE and JULIAN ZEDNER (*Ber.*, 1908, 41, 1948–1960. Compare Joffe and Geisel, *Abstr.*, 1906, ii, 228; Joannis, *ibid.*, ii, 161; 1907, i, 459; Kraus, *Abstr.*, 1907, ii, 935).—The boiling-point and the melting-point curves of solutions of lithium, sodium, and potassium in liquid ammonia at different concentrations have been plotted. The boiling-point curves at small concentrations are of the usual type, but

the b. p.'s of solutions containing more than 8 (atomic) % of the metal begin to rise rapidly, indicating possibly the existence of compounds.

In particular, the behaviour of sodium in ammonia has been examined at temperatures below the boiling points at atmospheric pressure. Above -46° , only one liquid phase exists at any concentration, but below this temperature, separation into two liquid phases or one solid and one liquid phase occurs. Evidence of the existence of compounds has not been obtained, except perhaps at the eutectic point, -111° , where the composition corresponds with the formula $\text{Na}(\text{NH}_3)_6$.

Saturated solutions of lithium, sodium, and potassium boil at temperatures which are practically the same as those at which Moissan first observed a reaction between the metal and liquid ammonia.
C. S.

Extraction of Potassium from Felspathic Rock. ALLERTON S. CUSHMAN and PREVOST HUBBARD (*J. Amer. Chem. Soc.*, 1908, 30, 779—797).—The object of the experiments was to obtain a remunerative process for extracting potassium from rocks for agricultural purposes. A certain amount of the potassium of felspars is dissolved by water when the mineral is finely ground, and the amount dissolved is increased by addition of substances such as ammonium salts, lime, and gypsum. Complete solution of the potassium can be effected by means of an electrolytic method, both with and without addition of hydrofluoric acid; the method would, however, probably be too costly for practical purposes. Attacking the silicates by means of potassium hydroxide or carbonate, &c., or with hydrofluoric acid, are suggested as possible methods which should receive further study.

Diagrams are given showing the amounts of potassium dissolved by water and the action of acids in relation to fineness and to duration of action. As regards the action of water, it is shown that the amount of potassium dissolved does not increase in exact ratio to the increase of surface area, probably owing to increased coagulation as the particles decrease in size.
N. H. J. M.

Polyiodides of Potassium, Rubidium, and Caesium. HARRY W. FOOTE and W. C. CHALKER (*Amer. Chem. J.*, 1908, 39, 364—367).—Aegg and Hamburger (*Abstr.*, 1906, i, 747) have made a study of the polyiodides of the alkali metals, and have concluded that the following salts exist as stable solids at 25° : KI_3 ; RbI_3 , RbI_4 , RbI_5 ; CsI_3 , CsI_4 , or CsI_5 , and CsI_6 . Johnson (*Trans.*, 1877, 249) has described the compound KI_3 , whilst Wells and Penfield (*Abstr.*, 1892, 773) and Wells and Wheeler (*Abstr.*, 1893, ii, 67, 68) have prepared the salts RbI_3 , CsI_3 , and CsI_5 , but were unable to obtain higher iodides of potassium than KI_3 .

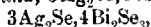
From experiments on the solubility relations of the caesium periodides, Foote (*Abstr.*, 1903, ii, 367) concluded that CsI_3 and CsI_5 were the only compounds found at the temperatures investigated. A similar study has now been made of the solubility relations of the polyiodides of potassium, rubidium, and caesium at 23° , and the composition of the residues has been determined. The results prove

the existence of the salts KI_3 , RbI_3 , CaI_2 , CsI_2 , and KI_2 , but do not give any indication of the formation of the compounds RbI_2 , RbI_3 , CsI_2 , and CsI_3 . E. G.

Explosion Produced by an Ordinary Reagent. CAMILLE MATIGNON (*Bull. Soc. chim.*, 1908, [iv], 3, 618—619).—On attempting to move a glass vessel containing an ammoniacal solution of silver oxide which had been left for twenty-four hours, a violent explosion occurred. This was found to be due to the formation of silver nitride, or products intermediate between this and the oxide, according to the equation $3AgOH + NH_3 = NAg_3 + 3H_2O$.

The mixture constitutes Berthollet's fulminating silver, and had dried on the surface of the glass. Such a solution should therefore be thrown away after use. J. C. C.

Compounds Formed by Silver Selenide with the Selenides of Arsenic, Antimony, and Bismuth. HENRI PÉLAGON (*Compt. rend.*, 1908, 146, 975—977).—The freezing-point curves of mixtures of silver selenide with the selenide of antimony or bismuth, obtained by plotting the number of mols. of the added selenide per 100 mols. of the silver selenide as abscissæ against the freezing point of the mixture as ordinates, are closely similar, and consist of four branches, showing two minima and one maximum; the latter corresponds with the freezing point of the compound, $3Ag_2Se, 4Sb_2Se_3$, f. p. 650° , or



f. p. 773° , respectively. The freezing-point curve of mixtures of silver and arsenic selenide shows a maximum corresponding with the freezing point of the compound $3Ag_2Se, 4As_2Se_3$.

Similar evidence was obtained of the existence of compounds of silver selenide with the lower selenides of antimony (Chrétien, *Abstr.*, 1906, ii, 550); these compounds are represented by the formulæ $SbSe_{\frac{1}{2}}Ag_2Se$, Sb_2Se_4, Ag_2Se , and $4Sb_2Se_3, 5Ag_2Se$ respectively.

M. A. W.

Chemical Properties of Calcium. HUGO ERDMANN and HEINRICH VAN DER SMISSEN (*Annalen*, 1908, 361, 32—68).—As calcium is now prepared technically on the large scale, it was thought of interest to undertake a systematic investigation of the chemical properties of the metal. The calcium employed in the experiments now described was chiefly filings from the electrolytic metal. For some experiments, crystalline calcium was prepared by reduction of calcium iodide by Moissan's method.

Whilst readily attacked by air or liquid nitrogen (Erdmann, *Abstr.*, 1906, ii, 349; Jordis and Rosenhaupt, *this vol.*, ii, 172), calcium is highly stable towards dry oxygen. Calcium oxide and mercury are formed only on prolonged heating of 1% calcium amalgam in a current of oxygen at $400-500^\circ$; mercuric oxide also is formed if the oxygen is ozonised. The formation of calcium peroxide could not be detected. On the other hand, calcium is oxidised so rapidly in presence of moisture that, whilst when cut under mercury the fresh surface of the metal is amalgamated instantaneously, a surface which has been

exposed to moist air for a quarter of a second is amalgamated only at 100–200°.

Contrary to statements in the literature, calcium hydride, whilst energetically attacked by water, is extremely stable towards anhydrous reagents. With certain precautions, calcium hydride is recommended as a source of pure hydrogen, as also for the preparation of hydrogen on the large scale.

Calcium nitride, Ca_3N_2 (Maqueune, Abstr., 1892, 776), is prepared by passing a current of nitrogen through fused calcium in an iron crucible, or by the action of liquid nitrogen on the metal. Contrary to Kaiser's statement (French Patent, 350966, 1905), ammonia is not formed when hydrogen is passed over calcium nitride or nitrogen over the hydride at 500–800° (compare Haber and Oordt, Abstr., 1905, ii, 159, 384, 814).

Moissan has shown (Abstr., 1899, i, 410; ii, 152, 153) that calcium reacts with ammonia at -78° to 20° , forming calcium ammooia, $\text{Ca}(\text{NH}_3)_4$, but at 500–1000°, forming calcium nitride and hydride, whilst an analogous derivative of methylamine cannot be obtained. It is now found that calcium reacts with ethylamine at 250–400°, yielding hydrogen, nitrogen, calcium nitride, calcium hydride, and carbon. On the other hand, calcium reacts with aromatic amines, forming compounds of the type $(\text{NHR})_2\text{Ca}$.

Calcium anilide, $(\text{NHPh})_2\text{Ca}$, prepared by heating calcium with aniline in an atmosphere of hydrogen at 200° , is obtained as a white, microcrystalline powder, D 1.17, which is insoluble in organic solvents, decomposes when exposed to moist air, explodes in dry oxygen, and yields aniline and calcium hydrate when treated with water, or aniline and calcium salts with acids. When treated with oxygen highly diluted with nitrogen at -20° , the anilide absorbs 1.3 atoms of oxygen for each atom of calcium, and forms a black, resinous mass of basic character. With ethyl iodide at the ordinary temperature, the anilide forms ethylaniline; with benzoyl chloride in ethereal solution, benzanilide; with gaseous carbonyl chloride, carbanilide; with carbon disulphide, thiocarbanilide; with sulphur dioxide, a yellow product, which evolves sulphur dioxide when heated; and with carbon dioxide, *calcium phenylcarbamate*, $(\text{NHPh}\cdot\text{CO}_2)_2\text{Ca}$. Heat is developed by the reactions with carbon disulphide, sulphur dioxide, and carbon dioxide. Calcium phenylcarbamate is formed also when calcium is heated with aniline at 250° in an atmosphere of carbon dioxide; when heated, it decomposes, forming calcium carbonate and carbanilide.

Calcium o-toluidide, $(\text{NH}\cdot\text{C}_6\text{H}_4)_2\text{Ca}$, formed from calcium and o-toluidine at 240° , resembles the anilide. It absorbs carbon dioxide, forming *calcium o-tolylcarbamate*, $(\text{C}_6\text{H}_4\text{O}_2\text{N})_2\text{Ca}$, which is decomposed by acids, forming carbon dioxide, o-toluidine, and the calcium salts, and, when heated, yields calcium carbonate and s-di-o-tolylcarbamide.

Calcium p-toluidide, formed from calcium and p-toluidine at 260° , absorbs carbon dioxide, forming *calcium p-tolylcarbamate*.

Calcium diphenylamide, $(\text{C}_6\text{H}_5)_2\text{N}\cdot\text{Ca}$, prepared from calcium and diphenylamine at 355° , is obtained as a white powder, which is attacked only slowly by dry oxygen, becomes green in presence of

dry air, decomposes, developing heat on exposure to moist air, and explodes in moist oxygen. It is attacked only slowly by water or dilute acids, but forms diphenylamine and calcium sulphate with concentrated sulphuric acid. It yields the following substances when treated with the reagents named.

With benzoyl chloride, diphenylbenzamide; with carbonyl chloride, tetraphenylcarbamide; with an excess of carbonyl chloride, diphenylcarbamyl chloride, and with carbon dioxide, *calcium diphenylcarbamate*, which is obtained as a white powder, and when heated yields tetraphenylcarbamide.

Calcium reacts with the naphthylamines at 280°, evolving hydrogen and small amounts of ammonia, and forming a yellow, brittle glass. At 240°, calcium and *p*-anisidine form a brown *product*, which becomes dark blue on exposure to air. Calcium reacts also with ethylaniline at 240°, forming a brown *product*, which is sensitive to light; with acetamide at 140°, forming a gelatinous *substance*, and with acetanilide at 200°, forming, amongst other products, acetaldehyde and anilide. Calcium and henizidine do not react at 420°.

Phenylhydrazine reacts with calcium slowly at 100° and rapidly at 140–160°, forming nitrogen, hydrogen, ammonia, benzene, aniline, and a white *powder*, $C_{13}H_{13}N_2Ca(?)$, which is attacked violently by dry oxygen, and absorbs carbon dioxide with development of heat.

Contrary to Moissan's statement (Abstr., 1900, ii, 76), calcium hydride does not react with sulphur dioxide or with acetylene (Abstr., 1899, ii, 153). When heated with calcium at 400°, fluorene evolves hydrogen and forms a black mass, but, under the same conditions, benzene, naphthalene, tetraphenylmethane, and acenaphthene remain unchanged. On the other hand, ethyl acetate reacts with calcium at 300°, or in presence of traces of alcohol at 156°.

Ethyl calciumacetoacetate, $(C_6H_5O_2)_2Ca$, formed from calcium and ethyl acetoacetate at 150°, is obtained as a white, crystalline powder, m. p. 215–220° (decomp.) if rapidly, or decomp. 180° if slowly, heated. Also, ethyl ethylacetoacetate reacts with calcium at 170°, evolving hydrogen. A pure product could not be obtained. Ethyl malonate and calcium evolve hydrogen at 160–180°, forming a yellow, flocculent *product*, which could not be purified. G. Y.

A New Calcium Silicide. L. HACKSPILL (*Bull. Soc. chim.*, 1908, [iv], 3, 619–621).—A new *calcium silicide*, Si_2Ca_3 , is obtained by heating to 1000° a mixture of calcium filings and powdered silicon compressed in a hole, 4–5 mm. diameter, bored in a calcium cylinder fitting in an iron test-tube, which is placed in a porcelain tube. On cooling, excess of calcium is removed by sugar solution, and the remaining slender needles are washed with alcohol and ether. The silicide is readily powdered, and has D_4^{20} 1.64. It is attacked by halogens in the cold, and by oxygen at a red heat. With dilute mineral acids, it is decomposed with evolution of spontaneously inflammable silicon hydrides. J. C. C.

Micrography of Cement. E. STERN (*Ber.*, 1908, 41, 1742–1745).—Hardened cements, or cements in the process of hardening, have

been examined micrographically in reflected light by the method employed for metals and alloys. The etched sections show the original cement particles, *A*, composed mainly of alite, and a portion, *B*, in which the process of hardening takes place; very little alteration in appearance occurs during the hardening process, although *B* slowly increases at the expense of *A*. The sections yield characteristic results when etched with alkalis, alcoholic hydrochloric acid, alcoholic iodine solution, or 25% hydrofluoric acid. Portland cement and iron-Portland cement can be distinguished by this micrographic process.

The action of salt solutions, sea-water, &c., has been examined, and also the effect of high temperature.

J. J. S.

Cæsium Dicalcium Sulphate. JOH. D'ANS (*Ber.*, 1908, 41, 1776—1777).—In continuation of his study of double sulphates (Abstr., 1906, ii, 751; 1907, ii, 168; this vol., ii, 104, 289), the author has prepared *cæsium dicalcium sulphate*, $\text{Ca}_2\text{Cs}_2(\text{SO}_4)_2$, by adding gypsum to a solution of cæsium sulphate. It forms crystals similar to those of ammonium and rubidium dicalcium sulphates, and is extremely stable, the stability increasing with the temperature. Attempts to prepare a salt analogous to syngenite, or a pentacalcium salt, have been unsuccessful. The temperature limit of stability of the calcium double sulphates falls as the mol. weight of the alkali sulphate increases. Whilst potassium syngenite is stable far above 100° , rubidium syngenite decomposes above about 40° ; on the other hand, whilst ammonium dicalcium sulphate exists only above 80° , cæsium dicalcium sulphate is formed below 0° .

A thallium calcium sulphate could not be prepared.

G. Y.

Neutral Triple Sulphates of Calcium. JOH. D'ANS (*Ber.*, 1908, 41, 1777—1779).—Only two neutral triple sulphates of calcium, the naturally-occurring polyhalite, $\text{Ca}_2\text{MgK}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ (Basch, Abstr., 1901, ii, 168), and krugite, $\text{Ca}_4\text{MgK}_2(\text{SO}_4)_6 \cdot 2\text{H}_2\text{O}$ (Geiger, Abstr., 1904, ii, 268), have been studied previously. The observation of the formation of a polyhalite, in which the magnesium is displaced by copper by the action of copper sulphate solution on potassium syngenite, has led the author to investigate the formation of such triple sulphates.

It is found that polyhalites, in which the magnesium is displaced by copper, cadmium, nickel, or zinc, and the potassium by ammonium, are formed when gypsum is boiled with suitably concentrated solutions of the other two sulphates. The synthetical salts crystallise more readily than the naturally-occurring triple sulphates; the *copper ammonium* and *copper potassium* salts are light blue. Analyses are quoted of the *dicalcium copper diammonium*, $\text{Ca}_2\text{Cu}(\text{NH}_4)_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$, and *dicalcium cadmium dipotassium*, $\text{Ca}_2\text{CdK}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$, sulphates.

These results have led to the synthesis of polyhalite by boiling gypsum, or a mixture of this with syngenite, with a concentrated solution of magnesium sulphate containing about 4% of potassium sulphate.

G. Y.

Composition of Artificial Magnesite Stone. FELIX CORNU (*Centr. Min.*, 1908, 305—310).—The basic refractory bricks used for

lining iron furnaces, which are made by igniting the coarsely crystalline magnesite (or rather breunnerite, since it contains $3.2 \pm 3.5\%$ iron) from Veitsch in Styria, were found to consist largely (94%) of a crystalline aggregate of grains of periclase together with some glassy material. Enclosed in the grains of periclase are skeletal growths of magnesioferrite.

L. J. S.

Amalgamated Zinc. CHARLES M. VAN DEVENTER (*Chem. Weekblad*, 1908, 5, 356—359).—A theoretical paper, reviewing the theories advanced to explain the lack of activity displayed by amalgamated zinc towards dilute sulphuric acid.

A. J. W.

New Reaction of Thallous Salts. FRITZ EPHRAIM (*Zeitsch. anorg. Chem.*, 1908, 58, 353—355).—A clear aqueous solution of antimony chloride and potassium iodide gives with an acid or neutral solution of any thallous salt a characteristic voluminous, orange to sennabar-red precipitate of the compound $3\text{TlI}_2\cdot 2\text{SbI}_3$. Thallous salts in a dilution of 1 in 20,000 can be detected in this way, but the compound cannot be used for the quantitative determination of thallous salts, as it is decomposed by water.

G. S.

Effect of Glass and Traces of Organic Substances on Mercuric Chloride Solution. WILLEM VAN RYN (*Pharm. Weekblad*, 1908, 45, 636—637).—Dilute aqueous solutions of mercuric chloride (1:4000 to 5000), preserved in corked bottles, are completely reduced in a few days either to a mixture of mercuric oxychloride and mercurous chloride or to mercurous chloride only. The author attributes the reduction to the action of the glass, of the cork, and of traces of organic matter in the solution.

A. J. W.

Resolution of Ytterbium into its Elements. CARL AUER VON WELSCHACH (*Monatsh.*, 1908, 29, 181—225).—It was stated in a previous communication (Abstr., 1907, ii, 26) that the fraction obtained during the separation of the elements of the ytterbium group, which should have contained pure ytterbium, gave a spark spectrum which differed considerably from the ytterbium spectrum; for instance, the four lines in the green, $\lambda = 5353.0$, 5347.4 , 5345.9 , and 5335.2 , so characteristic of ytterbium had almost disappeared. The conclusion was drawn therefore that the ytterbium had partly been resolved. At the same time, a fraction was obtained between the erbium and thulium fractions which gave a spectrum termed Ery. This fraction has been further investigated, and by repeated fractional precipitation of the oxalate by ammonium oxalate a fraction was finally obtained which gave a spark spectrum in which the lines which were missing or were very faint in the first-mentioned spectrum, for example, the four lines in the green, were exceedingly intense.

Large quantities of the fractions containing the two new substances were therefore carefully fractionated by repeated precipitation of the oxalates, and finally two fractions were obtained which could not be further resolved. It is proposed to name the two new elements so obtained *aldebaranium* (Ad) and *cassiopium* (Cp). Their atomic weights, determined by conversion of the oxides into sulphates, were found to

be $Ad = 172.9$ and $Cp = 174.23$ ($O = 16$). The two elements cannot be distinguished one from the other by chemical means; they, of course, possess the chemical properties ascribed to ytterbium.

The principal lines of the spark spectrum of aldebaranum are $\lambda = 5353.0, 5347.4, 5345.9, 5335.2, 4786.8, 4726.0, 4181.0, 3688.2, 3694.3, 3289.5$, and 2750.6 ; of cassiopeium, $\lambda = 6222.0, 6160.2, 5984.0, 5476.9, 5135.2, 4994.3, 4785.5, 4684.0, 4184.4, 3694.3, 3554.6, 3507.6, 3472.7, 3397.2, 3289.5, 2911.5, 2900.4, 2895.0$, and 2615.5 . The two spectra combined practically give the spectrum of ytterbium, but there are nevertheless some lines present in the spectrum of the latter, for example, $\lambda = 5104.6, 5067.4$, and 5009.7 , which do not appear in the spectra of aldebaranum or cassiopeium. It is therefore evident that ytterbium also contains a third unknown element.

The original contains a complete list of the wave-lengths of the lines of the spark spectra of ytterbium, aldebaranum, and cassiopeium, also reproductions of the photographs of these spectra. W. H. G.

Silicon-Aluminium Alloys. WALTER FRAENKEL (*Zeitsch. anorg. Chem.*, 1908, 58, 154—158).—The aluminium used in the investigation contained nearly 99% of the pure metal; the specimen of silicon contained 96.6% of that element and about 1% of aluminium.

The elements are miscible in all proportions in the fused state, and do not enter into chemical combination. The freezing-point curve consists of two branches; the eutectic mixture contains about 10% of silicon, and solidifies at 576° . Whether mixed crystals are formed could not be satisfactorily determined; if they exist, those rich in aluminium do not contain more than 0.5% of silicon, and those rich in the latter element not more than 2% of aluminium. There is some evidence that silicon, like bismuth, expands on solidification. G. S.

Aluminium Silicates. FRITZ ULFFERS (*J. pr. Chem.*, 1908, [ii], 77, 549—552. Compare Abstr., 1907, ii, 776).—Polemical. A reply to Jordis (this vol., ii, 291). G. Y.

Manganese and its Alloys with Carbon. A. STABELEI (*Metallurgie*, 1908, 5, 260—267, 281—288).—Manganese, prepared by the Goldschmidt method, contains 1.3% Si, 1.46% Al, and 1.03% Fe. The silicon may be removed by fusion with potassium permanganate, but the iron is less readily oxidised than the manganese, and, as the loss by volatilisation is considerable, dry refining of the manganese is impracticable.

In the investigation of the manganese-carbon alloys, the mixtures were fused in crucibles, lined with magnesite, in a current of nitrogen.

The maximum solubility of carbon in manganese at 2000° is 6.72% corresponding with the carbide, Mn_3C . The mixtures solidify to form a continuous series of mixed crystals, having a maximum freezing point at 1271° and 3.32% C, and falling to the freezing point of the carbide at 1217° . The metallographic examination of quenched alloys confirms the existence of mixed crystals, visible as polyhedra in alloys containing less than 3.32% C, and as long needles in alloys richer in carbon. At a lower temperature, rising from 817° at 0.72% C to

855° at 3.60% C, these crystals break up into other mixed crystals, one series of which is nearly pure manganese, and the other rich in carbide. Alloys containing more than 3.60% C have the same structure whether slowly cooled or quenched.

Manganese does not take up carbon when heated in sugar charcoal for twelve hours at 1100°.

Manganese carbide, Mn_3C , has D 6.888, and is readily oxidised. Alloys containing more than 3% of carbon fall to pieces at once in water, and even disintegrate spontaneously in closed vessels after a few weeks, apparently owing to the evolution of retained gas.

C. H. D.

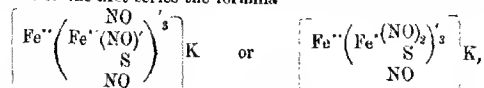
Preparation of Electrolytic Iron. RICHARD AMBERG (*Zeitsch. Elektrochem.*, 1908, 14, 326—328).—Electrolytic iron was prepared in quantities of 240 to 1000 grams by electrolysis of a solution of ferrous ammonium sulphate containing not less than 26 grams of iron per litre with a cathodic current density of 0.002 to 0.0065 ampere per sq. cm. With the highest current density, a stirrer was used. The anodes of wrought iron were enclosed in linen bags, and the surface of the bath protected from the air by a layer of solid paraffin. The iron, after removal of hydrogen, contained over 99.9% of iron, but difficulty was experienced with the anode mud.

T. E.

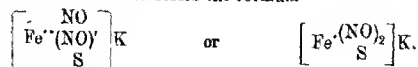
Optical Method for Determining the Relative Hardness of Contiguous Structural Elements of Alloys. M. K. CIGLER (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 584—591).—Soft iron nails were heated in boiling sulphur. Sections were prepared, and the hardness of the different parts determined by an optical method. The results show that the first product of the interaction of iron and sulphur at 448° is ferrous sulphide, which is afterwards converted into ferric sulphide by the further action of the sulphur.

T. H. P.

Probable Constitutional Formulae of the Ferronitrosulphides. ITALO BELLUCCI and PIETRO DE CESARIS (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 545—552. Compare this vol., ii, 499).—The authors have studied (1) the conversion of ferronitrosulphides of the first series into those of the second series, which takes place according to the equation $2[Fe(NO)_2S_3]K + 4KHO = 6[Fe(NO)_2S]K + Fe_2O_3 + N_2O + 2H_2O$, and (2) the reverse change, which is expressed by the equation $4[Fe(NO)_2S]K + CO_2 + 11_2O = [Fe(NO)_2S_3]K + H_2S + KNO + K_2CO_3$. Consideration of these results and of the products of decomposition of the anions $[Fe(NO)_2S_3]^-$ and $[Fe(NO)_2S]^-$ in alkaline and acid media (*loc. cit.*) leads the authors to propose for ferronitrosulphides of the first series the formula



and for those of the second series the formula



All the known reactions of the ferronitrosulphides are explained by either pair of these formulæ.

T. H. P.

Alloys of Lead and Cobalt. F. DUCELLIEZ (*Bull. Soc. chim.*, 1908, [iv], 3, 621—622).—Apparently homogeneous alloys of lead and cobalt can be obtained by subjecting mixtures of the two metals to hydraulic pressure, and then heating the masses so prepared at 1460° in magnesia crucibles in a current of hydrogen. Products made in this way and containing from 22.8% to 95.1% of cobalt behaved as mixtures of the two metals, and did not contain any definite compound. Vigouroux has already shown that, in like manner, nickel and lead form no definite compound (*Proc. verb. Soc. Sci. phys. nat., Bord.*, Nov. 21, 1907).

T. A. H.

Reduction and Oxidation of Nickel Oxide under the Ordinary and High Pressures. VLADIMIR IPATIEFF (*J. pr. Chem.*, 1908, [ii], 77, 513—532. Compare Moissan, *Abstr.*, 1881, 74).—A study of the part played by nickel oxide in the mechanism of catalytic reductions (*Abstr.*, 1907, i, 828). The results of experiments on the action of hydrogen on nickelic and nickelous oxides at varying temperatures and under different pressures are tabulated. It is found that nickelic oxide is reduced to nickel by hydrogen under the ordinary pressure at 190—200°, whereas nickelous oxide, which appears to be present always in commercial nickelic oxide, is not reduced under the ordinary pressure below 200°; but under high pressures it is reduced at 172°, unless first heated before the blowpipe, when reduction takes place only slowly at 250°.

If reduced below 270° and exposed to air at the temperature of the reduction, nickel inflames and is oxidised to nickelous oxide, but, if reduced at 270—280°, it is oxidised by dry air or oxygen only at 350°, or completely, forming nickelous oxide, at 400°, and can then be reduced by hydrogen under the ordinary pressure only at 300°. The temperature of oxidation of reduced nickel is lowered by the presence of moisture. Nickelous oxide is not oxidised by dry or moist air or oxygen under the ordinary or higher pressure within the temperature interval 220—480°.

Experiments on the reduction of the oxides of nickel by hydrogen under high pressures in presence of benzene show that, under these conditions, nickelic oxide is reduced to only a very slight extent at 250°, but the reduction of nickelous oxide takes place at the same temperature, 172°, as in the absence of benzene. If heated before the blowpipe, nickelous oxide reduces benzene catalytically only above 200°, and is itself only very slightly reduced.

These results are in agreement with the author's view that the catalyst in such reductions is nickelic oxide, and that the reduction is facilitated by the presence of moisture.

G. Y.

Isomerism of Chromium Salts. PAUL PFEIFFER (*Zeitsch. anorg. Chem.*, 1908, 58, 317—324. Compare this vol., i, 506, 507, 508).—The paper contains a summary and bibliography of the 29 types of isomerism which have so far been observed for chromium salts.

G. S.

Chromium Chlorosulphate. RUDOLF F. WEINLAND and TH. SCHUMANN (*Zeitsch. anorg. Chem.*, 1908, 53, 176—182. Compare Abstr., 1906, ii, 233; 1907, ii, 623).—A green chlorosulphate of chromium, $[\text{CrCl}_5\text{H}_2\text{O}]\text{SO}_4 \cdot 3\text{H}_2\text{O}$, in which the SO_4 group, but not the chlorine, is ionised, is already known (compare Recoura, Abstr., 1902, ii, 563; Weinland, *loc. cit.*). The authors have now prepared the isomeric compound $(\text{CrSO}_4 \cdot 5\text{H}_2\text{O})[\text{Cl}]$, in which the chlorine, but not the SO_4 , is present as ion, as follows. Violet chromium sulphate, $\text{Cr}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$, is heated at 80° until it loses $3\frac{1}{2}\text{H}_2\text{O}$ and is uniformly green, then dissolved in water, kept for three hours, cooled, and saturated with hydrogen chloride, when the salt in question separates as a green, crystalline powder.

When hydrogen chloride is led for a short time into a cooled saturated solution of the compound $[\text{CrCl}_5\text{H}_2\text{O}]\text{SO}_4 \cdot 3\text{H}_2\text{O}$, a salt of the formula $\text{CrCl}_2 \cdot 6\text{H}_2\text{O}$ separates in slender, bluish-green needles. As rather more than two-thirds of the chlorine is precipitated by silver nitrate in nitric acid solution, the salt is probably a monochlorochromium dichloride (compare Bjerrum, Abstr., 1907, ii, 622).

G. S.

Complex Molybdates of the Rare Earths. GIUSEPPE A. RABBIERI (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 540—545).—Conductivity and cryoscopic measurements of salts of the rare earths with strong acids (compare Muthmann, Abstr., 1898, ii, 586; Ley, Abstr., 1900, ii, 67; Meyer and Aufrecht, Abstr., 1904, ii, 175) show that, in aqueous solution, these salts are highly dissociated and hence only slightly hydrolysed. The rare earth metals have therefore a high electro-affinity, which is certainly greater than that of aluminium. The present paper describes the first of a series of investigations on the tendency of the rare earth metals to form complex ions, a tendency which is in inverse ratio to the electro-affinity.

Ammonium ceromolybdate, $(\text{NH}_4)_6\text{Ce}_2\text{Mo}_{12}\text{O}_{48} \cdot 24\text{H}_2\text{O}$, forms orange-red, monoclinic prisms, which give a solution of the same colour, whilst *ammonium lanthanomolybdate*, $(\text{NH}_4)_6\text{La}_2\text{Mo}_{12}\text{O}_{48} \cdot 24\text{H}_2\text{O}$, forms white, transparent crystals having a faint yellow tint.

T. H. P.

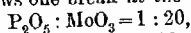
Silicides of Tungsten and of Molybdenum. EDOUARD DEFAQZ (*Bull. Soc. chim.*, 1908, [iv], 3, 577—578).—A question of priority (compare Abstr., 1907, ii, 475, 676; Hönigschmid, *Chem. Zeit.*, 1907, 31, 595; Abstr., 1907, ii, 877).

T. A. H.

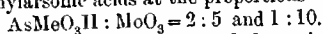
Complex Acids. I. ARTURIO MIOLATI and R. PIZZICHELLI (*J. pr. Chem.*, 1908, [ii], 77, 417—456).—A simple method for the study of the capacity of acids to form complex compounds with other acids has now been founded on the employment of the electrical conductivity as an indicator on the neutralisation of acids (Abstr., 1901, ii, 381). If an increasing amount of a substance is added to a solution of a second substance with which it reacts, some property of the solution, such as the specific electrical conductivity, must be a linear function of the proportion of the two substances in the solution. When the reaction is complete, a further addition of the substance must influence

the property measured to another extent, and hence a break must occur in the graph representing the rate of change. If two reactions take place successively, the graph must show two breaks, but, if the reactions are simultaneous, the property in question cannot be a linear function, and caution is required in interpreting the curve. In the light of these considerations, the authors have determined the electrical conductivities of solutions of molybdic acid containing varying amounts of other acids.

The graph for the electrical conductivity of solutions of molybdic and phosphoric acids shows one break at the proportion



whilst that for solutions of molybdic acid and disodium hydrogen phosphate has two breaks at the proportions $\text{P}_2\text{O}_5 : \text{MoO}_3 = 1 : 5$ and $1 : 16$. Breaks occur in the graph for solutions of molybdic and arsenic acids at $\text{As}_2\text{O}_3 : \text{MoO}_3 = 1 : 5$ and $1 : 20$, and in the graph for molybdic and methylarsonic acids at the proportions



Complex compounds of molybdic and methylarsonic acids have not been described. The graph for molybdic and cacodylic acids has one break at $\text{AsMe}_2\text{O}_2\text{H} : \text{MoO}_3 = 1 : 4$. The bearing of these observations on the existence of complex salts described by previous authors is discussed.

The basicity of phosphotungstic acid has been studied in the manner employed in the study of yellow phosphomolybdic acid (Abstr., 1904, ii, 263). Similar results are obtained, the electrical conductivity diminishing until 6 mols. of sodium hydroxide have been added, and then increasing steadily until the addition of 26 mols. of sodium hydroxide, the increase being still more rapid on further additions of alkali.

The paper closes with a long discussion of the constitution of the complex inorganic acids. Those containing 12MoO_3 or 12WO_3 may be conceived as derivatives of acids of the type $(\text{Mo})_6\text{H}_4$, in which the whole of the co-ordinated oxygen atoms are displaced by the bivalent anion Mo_2O_7 or W_2O_7 . The basicity of the resulting acid is the difference between the sum of the basicities of the co-ordinated, negative acid groups and the positive valency of the central atom. Hence phosphomolybdic, $[\text{P}(\text{Mo}_2\text{O}_7)_6]\text{X}_7$, phosphotungstic, $[\text{P}(\text{W}_2\text{O}_7)_6]\text{X}_7$, and arsenomolybdic, $[\text{As}(\text{Mo}_2\text{O}_7)_6]\text{X}_7$, acids are heptabasic, whereas silicomolybdic, $[\text{Si}(\text{Mo}_2\text{O}_7)_6]\text{X}_8$, silicotungstic, $[\text{Si}(\text{W}_2\text{O}_7)_6]\text{X}_8$, and cobaltomolybdic, $[\text{Co}(\text{Mo}_2\text{O}_7)_6]\text{X}_8$, acids are octabasic. If the complex acid contains less than twelve MoO_3 groups, the number of these is related to the number of hydroxyls in the anion, each hydroxyl being capable of combining with two MoO_3 groups. Thus the conductivity graph for mixtures of molybdic and dichloroplatinic acids has breaks at the proportions $\text{H}_2\text{PtCl}_2(\text{OH})_4 : \text{MoO}_3 = 1 : 2$ and $1 : 8$. G. Y.

Electrolytic Formation of Peroxygenated Compounds of Tin.
ANGELO COPPADORO (*Gazzetta*, 1908, 38, i, 489—508).—When concentrated alkali stannate solutions are electrolysed at low temperatures and with low current densities, perstannates are formed, owing to anodic oxidation. The proportion of perstannate formed is only

small, a condition of equilibrium being soon reached between the perstannate formed and decomposed. The addition of alkali fluoride to the electrolyte increases the rate of formation of the perstannate, but does not change the final equilibrium, so that the yield of perstannate remains unaltered. The presence of fluorine ions does not increase the anodic potential during electrolysis, and the conclusion is drawn that the fluorine enters into combination, forming either a stable perfluorine salt or an intermediate compound, which favours the oxidation of the stannate. The fact that perstannates are formed even at low current densities shows that their formation is due to secondary oxidation of the stannate by the nascent oxygen rather than by the union of two stannic anions. The yield of perstannate diminishes rapidly as the temperature of electrolysis rises. In solution at the ordinary temperature, the perstannates undergo gradual decomposition, yielding stannates.

T. H. P.

Phosphides of Titanium and Zirconium. JULIUS GEWECKE (*Annalen*, 1908, 361, 79—89. Compare Moissan, *Abstr.*, 1895, ii, 273; Chenevix, *Gmelin-Kraut*, II, 2, 15; Rose, *Ann. Phys. Chem.*, 1832, iii, 24, 141; Wöhler, *Annalen*, 1853, 87, 375).—When treated with hydrogen phosphide in the cold, titanium chloride forms a yellow, crystalline substance, which on being heated decomposes, yielding hydrogen phosphide, hydrogen chloride, and small amounts of titanium phosphide. A sketch is given of a convenient apparatus for carrying out these reactions. Titanium phosphide, TiP_3 , forms a brittle mass with metallic lustre, D_4^{25} 3.95, burns when heated in air or when fused with potassium nitrate, is a conductor of electricity, is insoluble in dilute or concentrated acids or alkalis, and is oxidised to only a small extent when boiled with *aqua regia* or heated with fuming nitric acid at 250—300°. When heated in chlorine, the phosphide burns, forming white fumes of titanium chloride and phosphorus pentachloride, which condense as a yellow sublimate, $TiCl_4.PCl_5$.

Zirconium phosphide, ZrP_3 , forms a glistering, grey mass, D_4^{25} 4.77, and closely resembles the titanium phosphide in its physical and chemical properties. When sublimed in a current of hydrogen over heated potassium phosphide, zirconium tetrachloride formed a mass containing potassium chloride, zirconium, phosphorus, and oxygen, which may have been derived from the presence of zirconium tetrachloride.

Silicon tetrachloride reacts with hydrogen phosphide, forming a zirconium phosphide, whereas thorium tetrachloride does not appear to react even at high temperatures.

G. Y.

Thorium Oxyfluoride and Fluoride. Ed. CHAUVENET (*Compt. rend.*, 1908, 146, 973—974).—When hydrated thorium oxide (Chydenius, *Jahresb.*, 1863, 194) or silicofluoride is heated at 100° in a platinum tube in a current of dry hydrogen fluoride, it is converted into the *oxyfluoride*, $ThOF_2$, a white, insoluble, amorphous powder yielding hydrogen fluoride on decomposition with sulphuric acid.

Thorium fluoride, ThF_4 (Moissan and Étard, *Abstr.*, 1896, ii, 422 :

Duboin, this vol., ii, 297), is obtained as an amorphous powder, which cannot be decomposed by sulphuric acid when thorium bromide or chloride is heated at 350–400° in a current of dry hydrogen fluoride.

M. A. W.

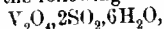
Mercuri-iodides of Thorium and Aluminium. ANDRÉ DUBOIS (*Compt. rend.*, 1908, 146, 1027–1028).—When thorium iodide, prepared by the action of hydriodic acid on thorium carbonate, and mercuric iodide are alternately dissolved in water at a gentle heat to saturation, the liquid on cooling deposits, first, mercuric iodide and then a mass of extremely deliquescent crystals of *thorium mercuri-iodide*, $\text{ThI}_4 \cdot 5\text{HgI}_2 \cdot 18\text{H}_2\text{O}$, easily decomposed by water, and quickly changed by exposure to air, becoming red. The mother liquor is dark brown in colour, owing to the presence of free iodine, and the latter is removed by shaking with mercurous iodide, giving a yellow liquid, D¹⁸⁹ 3512.

It has been shown previously that a saturated solution of mercuric iodide in aluminium iodide solution deposits an oxyiodide when left in dry air (Abstr., 1907, ii, 955). The mother liquor from this experiment, kept since then in the presence of anhydrous baryta, has deposited a very small quantity of elongated prisms of *aluminium mercuri-iodide*, $\text{AlI}_3 \cdot \text{HgI}_2 \cdot 8\text{H}_2\text{O}$, which is extraordinarily deliquescent, but dissolves in water without decomposition.

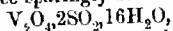
E. H.

Hypovanadic Acid and Some of its Compounds. GUSTAVE GAIN (*Ann. Chim. Phys.*, 1908, [viii], 14, 224–228).—A résumé of work already published, with additional observations (compare Abstr., 1907, ii, 32, 97, 558, 627; 1908, ii, 284). The two isomeric hydrates of hypovanadic acid dissolve readily in dilute aqueous solutions of hydrogen chloride or hydrogen bromide, and by evaporation the corresponding halogen salts are obtained in well-defined crystals (compare Guyard, Abstr., this Journ., 1876, ii, 173; Crow, *ibid.*, 453). The chloride, $\text{VO}_2\text{Cl}_2 \cdot 8\text{H}_2\text{O}$, is deep green when prepared from the green hydrate, but is blue when obtained from the rose hydrate. $\text{VO}_2\text{Br}_2 \cdot 5\text{H}_2\text{O}$, and forms large, rectangular tablets; an aqueous solution is intensely red, but becomes deep blue on the addition of hydrogen bromide in excess. The iodide was not obtained sufficiently pure for analysis; it forms a red aqueous solution turning blue on the addition of hydrogen iodide.

When the mixture of oxides (V_2O_3 and V_2O_5) resulting from the calcination of ammonium vanadate is treated in boiling aqueous solution with sulphur dioxide, a blue liquid is obtained, from which, under suitable conditions, the following salts can be isolated:



a blue, crystalline crust soluble in water; $\text{V}_2\text{O}_5 \cdot \text{SO}_2 \cdot 4\frac{1}{2}\text{H}_2\text{O}$, a deep green, amorphous substance sparingly soluble in cold water;



small, sky-blue crystals; $\text{V}_2\text{O}_5 \cdot 2\text{SO}_2 \cdot 8\text{H}_2\text{O}$, blue crystals. An aqueous solution of selenious acid dissolves the hydrate of hypovanadic acid, and, by allowing the solution to evaporate, pale blue, microscopic crystals of $\text{V}_2\text{O}_5 \cdot 2\text{SeO}_2 \cdot 4\text{H}_2\text{O}$ are obtained.

The author has also succeeded in obtaining a number of definite crystalline compounds by the union of hypovanadic acid with sulphuric acid. Some of these have already been described by Gerland and by Crow (*loc. cit.*), although only in the gummy or amorphous condition (compare Koppel, *Abstr.*, 1902, ii, 85; 1903, ii, 551). A description of the following salts is given: $V_2O_4 \cdot 2SO_3 \cdot 3H_2O$, elongated, deep blue prisms; $V_2O_4 \cdot 2SO_3 \cdot 5H_2O$, very bright blue, microscopic crystals; $V_2O_4 \cdot 4 \cdot 5SO_3 \cdot 11H_2O$ and $V_2O_4 \cdot 5SO_3 \cdot 12H_2O$ are very hygroscopic, blue, microcrystalline powders; $V_2O_4 \cdot 2 \cdot 5SO_3 \cdot 9H_2O$, azure-blue crystals; on ignition V_2O_5 is obtained; $V_2O_4 \cdot 3SO_3 \cdot 10H_2O$, turquoise-blue crystals; $V_2O_4 \cdot 3 \cdot 5SO_3 \cdot 10H_2O$, stable, bluish-green crystals. A new *selenate* has also been obtained in the form of a blue, microcrystalline powder having the composition $V_2O_4 \cdot 3 \cdot 5SeO_3 \cdot 7H_2O$.

Hypovanadic acid dissolves in nitric acid, forming a blue solution, but, when allowed to evaporate, this deposits the red hydrate of vanadic acid. A nitrate could not be obtained. The following nitrites are obtained by dissolving $V_2O_4 \cdot 2H_2O$ in aqueous solutions of the alkali nitrites: $(\bar{V}_2O_4 \cdot N_2O_3) \cdot (K_2O \cdot N_2O_3) \cdot 4H_2O$, colourless, regular hexagonal prisms; $[\bar{V}_2O_4 \cdot N_2O_3] \cdot (NH_4)_2O \cdot N_2O_3 \cdot 6H_2O$, pale yellow prisms. The corresponding *sodium* salt is obtained as a colourless, very unstable powder.

Hypovanadic acid unites with many organic acids, forming stable salts. The *formate*, $V_2O_4 \cdot (CHO_2)_2 \cdot 2H_2O$, is obtained as azure-blue crystals, which are less soluble in alcohol than in water. The *acetate*, $V_2O_4 \cdot (C_2H_3O_2)_2 \cdot 5H_2O$, is a greenish-blue, crystalline mass. The *oxalate*, $V_2O_4 \cdot (C_2O_4)_2 \cdot 7H_2O$, forms elongated, greenish-blue prisms. The *malonate* and *sulciylate* are blue, whilst the *succinate* is green.

The following new double sulphites have been prepared by treating the alkali hydrogen sulphites with an aqueous solution of hypovanadic acid: $3(V_2O_4 \cdot SO_3) \cdot 2(K_2O \cdot SO_3) \cdot 5H_2O$, small, blue crystals;

$2(\bar{V}_2O_4 \cdot SO_3) \cdot (K_2O \cdot SO_3) \cdot 2H_2O$, large, deep blue crystals; $(V_2O_4 \cdot 2SO_3) \cdot 2[(NH_4)_2O \cdot SO_3] \cdot 2H_2O$, well-formed, greenish-blue crystals; $5(V_2O_4 \cdot SO_3) \cdot 2[(NH_4)_2O \cdot SO_3] \cdot 16H_2O$, a bluish-green substance, rapidly turning brown;

$2(V_2O_4 \cdot SO_3) \cdot (Rh_2O \cdot SO_3) \cdot 4H_2O$, brilliant azure-blue crystals; $(V_2O_4 \cdot SO_3) \cdot 3(Tl_2O \cdot SO_3) \cdot 4H_2O$, emerald-green plates; $2(V_2O_4 \cdot SO_3) \cdot (Na_2O \cdot SO_3) \cdot 4H_2O$, bright green crystals, sparingly soluble in cold water.

The paper contains an account of the methods adopted for the analysis of the foregoing compounds.

W. O. W.

Action of Potassium Iodide and Hydrochloric Acid on Antimonic Acid. A. KOLB and R. FORMALS (*Zeitsch. anorg. Chem.*, 1908, 58, 189—201. Compare Youtz, *Abstr.*, 1904, ii, 159).—The oxidation of hydriodic acid by antimonic acid in the presence of hydrochloric acid according to the equation $Sb_2O_3 + 4HI \rightleftharpoons Sb_2O_5 + 2H_2O + 2I_2$ is a reversible reaction, and the same equilibrium point can be reached from both sides. The influence of varying concentrations of the reacting substances and of certain other compounds on the equilibrium point has been investigated systematically. When potassium iodide and especially hydrochloric acid are used in considerable excess,

the reaction is practically complete in the direction indicated by the upper arrow, which is of importance for the volumetric estimation of antimony compounds. Tartaric acid diminished the amount of iodine set free, and neutral salts increase it, as does rise of temperature. If cadmium iodide is used instead of potassium iodide, less iodine is set free.

The probable mechanism of the reaction is discussed.

G. S.

Hardness of Alloys. III. ALEXIS V. SAPOSHNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 665—673. Compare Abstr., 1907, ii, 869).—The hardness curve for alloys of antimony and bismuth exhibits a maximum at the composition $Sb_{1.0}Bi$, but does not indicate whether or not these two metals form a continuous series of solid solutions (compare Hüttner and Tammann, Abstr., 1905, ii, 327). The hardness curve for aluminium-tin alloys has also been constructed. The hardness falls rapidly as the percentage of tin present increases from 0 to 30, then rises to reach a maximum for 40% of tin, falls again, and attains another maximum very nearly at the composition $AlSn$.

T. H. P.

Atomic Weight of Bismuth. II. Synthesis of Bismuth Oxide. ALEXANDER GUTBIER and LOTHAR BIRCKENBACH (*J. pr. Chem.*, 1908, [ii], 77, 457—471. Compare Abstr., 1906, ii, 92).—Bismuth oxide has been formed by the action of nitric acid on three specimens of bismuth: (a) prepared by Schneider's process (Abstr., 1893, ii, 114); (b) prepared by a modification of Classen's method (Abstr., 1890, 706; 1891, 525; 1892, 20), and (c) a specimen supplied by Classen. Four experiments with (a) gave the mean value $Bi = 208.03$; four with (b) gave $Bi = 207.99$, whilst two with (c) gave $Bi = 208.00$. The extrema values obtained were $Bi = 207.88$ and $Bi = 208.20$. The value 208.0 ($O = 16$), which is now recommended as the atomic weight of bismuth, is in agreement with the joint results of the work of Schneider (*loc. cit.*) and Löwe (Abstr., 1884, 558).

G. Y.

Electrolysis of Bismuth Salt Solutions. ALEXANDER GUTBIER, LOTHAR BIRCKENBACH, and R. BENZ (*Chem. Zentr.*, 1908, i, 1256; from *Sitzungsber. Erlangen Physik-Med. Soc.*, 39, 173—175).—The previously observed bronze-coloured coating which covers the anode in a bismuth solution, and settles as small, lustrous plates to the bottom of the vessel, becomes redissolved on continuing the electrolysis. It is, however, formed in largest quantities from a solution of 20 grams of bismuth in 200 c.c. of nitric acid (D 1.4) diluted to 1500 c.c. with water containing 300 c.c. of concentrated ammonia solution in 2 litres, using $1.0-1.5^{-2}$ amp./qem. When the electrolyte is slowly replaced by water, the metallic lustre of this substance suddenly disappears, and a light brown, amorphous powder remains, consisting of 97.93% Bi_2O_3 with about 2% active oxygen.

J. V. E.

Optical Properties of Colloidal Gold Solutions. WALTER STEUBINO (*Ann. Physik.*, 1908, [iv], 26, 329—371).—When gold chloride solutions are reduced by means of hydrazine, red, blue, or violet

colloidal solutions of gold may be obtained. The solutions are very stable, and the colour depends on the temperature, the concentration, and the rapidity with which the reducing agent is mixed with the gold solution. The blue and red solutions both contain particles of uniform size, and both colours are given by solutions which contain particles of very different sizes. The colour of the colloidal gold does not therefore depend on the size of the particles, but there appear to be two distinct kinds of particles, the one giving rise to the red, and the other to the blue colour. The violet solutions contain both kinds of particles.

The author describes a method of measuring the light emitted laterally from the colloidal solutions when these are subjected to the influence of rays in a particular direction. This diffused light represents a very small fraction of the incident light, which is apparently absorbed. It is plane polarised to a large extent, and in the case of the light emitted at right angles to the direction of the incident beam, the proportion of plane polarised light has a maximum value of 90%.

When examined in the ultra-microscope by means of polarised light, the red and blue solutions exhibit considerable differences, and these are supposed to be due to differences in the geometrical form of the two kinds of particles. The laterally emitted light from the red solutions exhibits a maximum intensity in the region $560-570\ \mu\mu$; that from the blue solutions a feeble maximum at $570\ \mu\mu$ and a more strongly pronounced one in the red region. Violet solutions behave like a mixture of the red and blue solutions. A maximum of absorption is shown by red solutions at $525-530\ \mu\mu$, and a minimum by blue solutions at $490\ \mu\mu$; the absorption effects of the blue solutions are, however, not so sharply defined as those of the red.

Greyish-green colloidal solutions of gold have also been obtained by reduction with hydrazine in presence of a little potassium hydroxide. These solutions emit very little light laterally, and show fairly uniform absorption. It is supposed that the particles in these solutions are formed by condensation of the particles which give rise to the red and blue colours.

H. M. D.

Action of Silver Nitrate on Chloroauric Acid and the Preparation of Fulminating Gold. JULES JACOBSEN (*Compt. rend.*, 1908, 146, 1213-1214).—On adding silver nitrate to a solution of chloroauric acid, a brown precipitate is obtained according to the equation $\text{HAuCl}_4 + 4\text{AgNO}_3 + 3\text{H}_2\text{O} = \text{Au(OH)}_3 + 4\text{AgCl} + 4\text{HNO}_3$.

By the action of ammonia, this is converted into fulminating gold, which has the formula $\text{Au(OH)}_2 \cdot \text{NH}_2$ or $(\text{AuN}, 2\text{H}_2\text{O}) \cdot \text{H}_2\text{O}$. The substance, when washed with aqueous ammonia, followed by water, alcohol, and ether, and dried at a low temperature, explodes violently when touched with a knife. The explosion takes effect in a downward direction. On boiling fulminating gold with potassium hydroxide, a blackish-brown, flocculent product is obtained, which is still more explosive, and probably has the composition $\text{Au(OH)}_2 \cdot \text{NH} \cdot \text{Au(OH)}_3$.

J. C. C.

Passivity of Platinum. RUDOLF RUER (*Zeitsch. Elektrochem.*, 1908, 14, 309-314).—Previous experiments (*Abstr.*, 1903, ii, 407)

led to the view that the insolubility of a platinum anode was due to a coating of a peroxide. The coatings observed by Marie (Abstr., 1907, ii, 698) may be the peroxide in question. Further experiments show that the coating is formed with pure platinum in sulphuric acid containing from $2\frac{1}{2}$ to 10% of the acid. In stronger acids, no visible coating is formed. The coating is yellow to brown in colour; it is insoluble in cold sulphuric acid alone, but dissolves in presence of a reducing agent. It is a good conductor of electricity. The potential of a coated electrode is the same as that of one saturated with oxygen; it falls gradually to the potential of platinum charged with atmospheric oxygen. The coating has therefore the properties of the hypothetical peroxide, but, since it is not formed in 50% sulphuric acid and, in fact, dissolves when a coated plate is used as anode in acid of this strength, it cannot explain the insolubility of platinum in the strong acid.

T. E.

Definite Compounds of Silicon and Palladium. PAUL LEBEAU and PIERRE JOLIBOIS (*Compt. rend.*, 1908, 146, 1028—1031).—Boussingault has shown (Abstr., 1876, 47; 1879, 286) that palladium combines with silicon to the extent of 3.9%. When an intimate mixture of palladium and crystallised silicon is introduced into a porcelain crucible heated by means of a blowpipe, a contraction first occurs, and then, at 500—600°, combination is produced, accompanied by a bright incandescence and sufficient elevation of the temperature to cause complete fusion. The fusion temperature of mixtures of silicon and palladium varies largely with the content of silicon. With an increasing proportion of silicon, the m. p. falls from 1587° for pure palladium to the minimum 670°, corresponding with 6% of silicon; it then rises rapidly to the maximum 1400° for 11.76% of silicon (corresponding with SiPd_2); the m. p. then again falls, reaching a second minimum of 750° for 16% of silicon, and afterwards rising to a second maximum of 990° for 21% of silicon (corresponding with SiPd). With 25% of silicon there occurs another minimum of 825°, corresponding with an eutectic, and then the m. p. rises gradually to that of pure silicon. Observation of the rate of cooling of the mixtures shows that, for all those containing less than 20% of silicon, a well-defined slackening takes place, followed by a recalescence, the rise in temperature being sufficient to raise the mass to a bright red heat. The increase in incandescence so observed starts at a point in the mass and spreads in a manner similar to the crystallisation of a super-saturated solution, and the similarity in the two phenomena is further shown by the fact that the recalescence is prevented by contact of the mixture at the commencement of solidification with a small fragment of a similar ingot previously prepared. The behaviour, on cooling, of mixtures containing more than 21% of silicon, indicates the presence of the eutectic ($\text{SiPd}-\text{Si}$).

Comparison of different ingots which have undergone recalescence with the same products, tempered before the appearance of this phenomenon, reveals an interesting difference in structure. In the latter case, two homogeneous constituents are always observed, and are very easily distinguished by oxidation. When, however, recal-

escence has occurred, the more oxidisable constituent is besprinkled with small crystals.

The ingots corresponding with the compositions SiPd_2 and SiPd are both homogeneous, but only the latter silicide has been isolated in a crystalline form. When ingots containing above 60% of silicon are treated with dilute potash, the free silicon dissolves, leaving small, very brilliant, bluish-grey fragments of *palladium silicide*, SiPd , D¹⁵ 7.31, which, when hot, is attacked by fluorine and chlorine, is superficially oxidised by oxygen at a dull red heat, is attacked by cold nitric acid and aqua regia, but not by hydrochloric or sulphuric acid, and is slowly attacked by alkali hydroxides.

E. H.

Mineralogical Chemistry.

Proustite and Argentite from Colorado. FRANK R. VAN HORN (*Amer. J. Sci.*, 1908, [iv], 25, 507—508).—A vein of argenteiferous galena occurring in the California or Bell mine near Montezuma in Summit Co., Colorado, contains blende and chalybite together with some proustite (anal. I), and argentite (anal. II); the last two are massive and intimately intermixed with quartz:

	Ag.	As.	Sb.	S.	Insol.	Total.
I.	67.60	13.85	0.93	17.40	—	99.78
II.	83.57	—	—	12.66	3.62	99.85

L. J. S.

Composition of Certain Chilean Caliches. FRANZ W. DAFERT [with A. HALLA and R. WASCHATA] (*Monatsh.*, 1908, 29, 235—244).—The results of complete analyses of several samples of natural Chili saltpetre from Santa Clara are recorded. It is found that, although several caliches contain perchlorate, there are others which do not, whilst all contain more or less iodate. As a rule, the caliches rich in sodium nitrate also contain considerable quantities of potassium nitrate and small amounts of chromate.

The author discusses the bearing of his results on the various theories which have been put forward to explain the formation of saltpetre deposits.

W. H. G.

Paligorskite Group. A. FERSMANN (*Bull. Acad. Sci. St. Petersburg*, 1908, [vi], 637—666).—The author makes a critical comparison of all the analytical data published concerning the members of the paligorskite group, which he divides into the following classes: (1) Paramontmorillite, having the general composition $\text{H}_{12}\text{Al}_2\text{Si}_4\text{O}_{17}$; (2) α -paligorskite, $\text{H}_{22}\text{Mg}_2\text{Al}_4\text{Si}_{11}\text{O}_{46}$; (3) β -paligorskite, $\text{H}_{30}\text{Mg}_3\text{Al}_3\text{Si}_7\text{O}_{59}$; (4) α -pilotite, $\text{H}_{28}\text{Mg}_4\text{Al}_2\text{Si}_{10}\text{O}_{41}$; (5) β -pilotite, $\text{H}_{36}\text{Mg}_6\text{Al}_3\text{Si}_9\text{O}_{53}$; (6) parasepiolite, $\text{H}_2\text{Mg}_2\text{Si}_2\text{O}_{12}$; (7) ferruginous paligorskite. The

arrangement under this classification of the minerals known as mountain leather, mountain cork, lassalite, morencite, hydrous anthophyllite, &c., is explained.

The constitution of the basic series of the paligorskite group may be explained by the assumption of an orthosilicate (*A*) in the nucleus and an aluminosilicate or ferrisilicate (*B*) in the side-chain, the relations between these two silicates being expressed by simple whole numbers. In the extreme members of the series, there may be a deviation from these relations, owing to the presence of other silicates in varying proportions. The analytical numbers indicate that the group cannot consist of isomorphous mixtures of the two silicates, *A* and *B*, neither is the constitution in accord with an equivalent substitution of the magnesia of sepiolite by alumina.

T. H. P.

A New Variety of Paragonite Mica. PHILIPPE BARBIER (*Compt. rend.*, 1908, 146, 1220—1221).—A specimen of silvery mica, resembling muscovite in appearance, from Mesvres, near Autun, was analysed with the following results: loss on ignition, 4.60 (fluorine is absent); the calcined material gave:

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	K ₂ O.	Na ₂ O.	Li ₂ O.	Total.
49.18	36.56	2.19	3.12	7.63	1.26	99.94

The mineral is therefore a lithium-bearing variety of soda-mica, and for it the name *hallerite* is proposed.

L. J. S.

Gedrite from Canada. N. NORTON EVANS and J. AUSTEN BANCROFT (*Amer. J. Sci.*, 1908, [iv], 25, 509—512).—Gedrite, the aluminous variety of anthophyllite, occurs abundantly as a constituent of amphibolite in the township of Harcourt, Haliburton Co., Ontario. The amphibolite is associated with limestone and granite of Laurentian age, and contains, in addition to anthophyllite, garnet and cordierite, with subordinate amounts of quartz, biotite, iron-ore, and rutile. The anthophyllite has the form of sheaves of long, narrow crystals of a delicate clove-brown colour and characteristic pleochroism; it is optically negative with straight extinction. Analysis of material separated from the powdered rock by means of an electromagnet and heavy liquids gave the following results, agreeing with Rammeisberg's formula $4R\text{SiO}_3 \cdot \text{Al}_2\text{O}_3$, where $R = \text{Mg, Fe, H}_2$:

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.	H ₂ O.	K ₂ O, Na ₂ O.	Total.
44.32	16.04	2.80	16.88	0.09	0.77	15.95	1.31	1.86	100.02

The mineral is thus very similar to the original gedrite from Gêdres, in the Pyrenees. Neither anthophyllite nor cordierite have before been recorded from Canada.

L. J. S.

Delorenzite, a New Mineral. FERRUCCIO ZAMBONINI (*Zeitsch. Kryst. Min.*, 1908, 45, 76—81*).—The mineral occurs associated with struverite (this vol., ii, 398) in the pegmatite of Craveggia, Piedmont. The crystals are orthorhombic [$a:b:c = 0.3375:1:0.3412$], with prismatic habit closely resembling polycrase; they are black and opaque, but thin splinters are brown and isotropic. The fracture is conchoidal, with a brilliant pitchy to resinous lustre. Hardness

* and *Rend. Accad. Sci. Fis. Mat. Napoli*, 1908, [iii], 14, 113—118.

5½—6; D about 4·7; the mineral is strongly radioactive. Analysis by J. S. Stérba gave:

TiO ₂	SnO ₂	UO ₂	Y ₂ O ₃	FeO.	Total.
66·03	4·33	9·87	14·63	4·25	99·11

This corresponds with the formula $2\text{FeO} \cdot \text{UO}_2 \cdot 2\text{Y}_2\text{O}_3 \cdot 24\text{TiO}_2$, or written as a metatitanate, $2\text{FeTiO}_3 \cdot \text{U}(\text{TiO}_3)_2 \cdot 2\text{Y}_2(\text{TiO}_3)_3 \cdot 7(\text{TiO})\text{TiO}_3$.

The new mineral is thus nearer to ytrocraasite (Abstr., 1907, ii, 103) than to polycrase in composition. L. J. S.

Physiological Chemistry.

Influence of the Amount of Carbon Dioxide in the Respired Air on the Changes in Weight of Butterfly Pupæ. MARIA (GRÄFIN) VON LINDEN (*Bied. Zentr.*, 1908, 37, 427—429; from *Arch. Physiol.*, 1907, 162. Compare Abstr., 1906, ii, 95).—Experiments with two varieties of chrysalides show that carbon dioxide is absorbed, and that their existence as chrysalides is more prolonged in an atmosphere rich in carbon dioxide than in air. Carbon dioxide does not act as a narcotic, but acts rather as a stimulant, without, however, causing loss of weight, and the conclusion is drawn that carbon dioxide is a direct nutrient. N. H. J. M.

The Influence of the Reaction of Blood-plasma on the Formation of Fibrin. GUSTAVE PATEIN (*J. Pharm. Chim.*, 1908, [vi], 27, 518—522).—The addition of salts of calcium to an oxalated plasma produces no coagulum if the mixture is first made acid with acetic acid. The addition of alkalis produces the coagulum as soon as the reaction of the mixture is alkaline, provided that the mixture has not remained acid for very long. If, however, the mixture of oxalated plasma, calcium salt, and acetic acid has stood for a day, the addition of alkali fails to produce a coagulum. In this case, coagulation can be made to take place by the addition of normal serum. The fibrin ferment seems to have been destroyed by remaining for a long time in acid solution. S. B. S.

Albumose in the Blood. EMIL ABDERHALDEN (*Biochem. Zeitsch.*, 1908, 10, 277—282).—Polemical mainly against Freund. The present author withdraws none of his previous statements regarding the absence of albumoses in blood, blood-serum, and blood-plasma. W. D. H.

Origin of the Saccharifying Power of Human Saliva. W. METHEZAT (*Bull. Soc. chim.*, 1908, [iv], 3, 711—713).—Preparations of saliva extracted under aseptic conditions from the parotid and submaxillary glands are shown to possess the property of saccharifying

starch mucilage, that from the parotid gland being the more active. A mixture of the two secretions has a saccharifying power approximately the mean of those due to the two acting separately, and similar to that of ordinary saliva. The hydrolysis of starch by the latter is therefore due to a diastase (ptyalin) of glandular origin, and not to the action of bacteria occurring in the mouth (compare Duclaux, *Traité de Microbiologie*, 1899, 2).

T. A. H.

The Diastase in Cat's Saliva. ANTON J. CARLSON and J. G. RYAN (*Amer. J. Physiol.*, 1908, 22, 1—15).—Diastase is present in the blood in greater concentration than in the saliva; an increase in salivary diastase occurs after intravenous injection of human ptyalin and pancreatic amylase. Concentration of organic solids and of salivary diastase vary together. There is more diastase in the submaxillary than in the parotid saliva. These results were obtained by experiments on the cat; a few experiments made on dogs confirm them.

W. D. H.

Milk Curdling in the Infant's Stomach. ALOIS KREIDL and ALFRED NEUMANN (*Zentr. Physiol.*, 1908, 22, 133—136).—In the stomach of the sucking child and animal, rennin is present, and causes curdling of various kinds of milk. Whether curdling of human milk takes place was not observed directly, but it probably does, for the juice contains both acid and rennin, and curdles human milk *in vitro*.

W. D. H.

Remarks on Aron and Sebauer's Work on the Nutritive Value of Calcium Salts. ARNOLD ORGLER (*Biochem. Zeitsch.*, 1908, 10, 236—239. Compare this vol., ii, 208).—A criticism of Aron and Sebauer's methods and results.

W. D. H.

Specific Dynamic Action of Proteins. NATHAN ZUNTZ (*Zentr. Physiol.*, 1908, 22, 67—68).—The views of Graham Lusk (this vol., ii, 574) on this question are criticised. The heat value of lactic acid in the body is greater, not less, than that of alanine if allowance is made for the unburnt nitrogenous residue it yields. The work of the alimentary canal during digestion, involving as it does muscular and glandular activity lasting for many hours, cannot be a negligible factor in metabolism.

W. D. H.

Metabolism of Injected Proteins, Immunity and Hypersensitiveness. ULRICH FRIEDEMANN and S. ISAAC (*Chem. Zentr.*, 1908, 1, 967; from *Zeitsch. exp. Path. Ther.*, 1907, 4, 830—866).—The authors, in continuation of their former work (*ibid.*, 1905, 1, 573), have sought an explanation of the fate of proteins injected into the organism of dogs and of larger herbivora (goats and sheep). They found that during starvation such proteins cause a general rise in protein decomposition, such as follows protein administration by the alimentary tract. The increased nitrogen excretion will follow the injection of sera, either of the same or of other animals, as well as egg-proteins. In the case of dogs in nitrogenous equilibrium, protein injection on carbohydrate-free diet

causes increased protein decomposition, which can be inhibited by the addition of carbohydrates to the diet. The fact that proteins of different origin exert the same influence on nitrogenous excretion stands in contrast with their behaviour when tested by biological methods (precipitin and complement reactions). The parallelism between the nutrition phenomena and these biological phenomena is entirely wanting, for precipitins can be detected in the blood long after the injected proteins are eliminated from the body. From the facts, the authors conclude that the precipitable substances circulating in the serum are not identical with the injected protein.

The authors also noticed a characteristic phenomenon of hypersensitiveness in the case of dogs, in that a second injection following a preliminary injection of the same quantity of substance often causes acute intoxication leading to a fatal result. They ascribe this to a sudden inundation of the organism with toxic metabolism products, and compare this phenomena with what happens in diabetic coma, uremia, and the alimentary intoxication observed by Finkelstein in infants.

S. B. S.

Proteid Minimum in the Food of Cows. (*Bied. Zentr.*, 1908, 37, 393-413; from 60th and 63rd *Ber. Dänisch. Versuchslab.*, 1906 and 1907).—Nine cows were fed with hay (2.5 kilos.), straw (3.7-4.88 kilos.), and with different amounts of roots (increasing from 30 kilos. in the first period to 45 kilos. in the seventh) and cotton cake (decreasing from 2.5 to 1.5 kilos.). The amount of water consumed diminished as the amount of roots increased, so that the percentage of water in the total food remained about the same (80.8-82.5%). The food contained in the first period 221 grams of protein and 31 grams of amide nitrogen; in the fourth period, 128 and 35 grams respectively. The effect of reducing the amount of nitrogen, is diminution of nitrogen in the faeces and especially in the urine; the amount of excrement remained the same. The percentage of nitrogen in the milk was not altered, but the amount of milk was reduced. The first result of reducing the supply of nitrogen is to diminish the nitrogen of the urine, then that of the faeces, and thirdly that of the milk. When the amount is further reduced, nitrogen from the body is utilised for milk production for a short time, after which the yield of milk rapidly falls. Provided the amount of food is sufficient, the composition is unimportant, and may vary from year to year according to the magnitude of the crops, deficient crops being supplemented with suitable amounts of cake, &c.

Protein nitrogen must be given in sufficient quantity to correspond with the amounts in milk and faeces. Otherwise, even in presence of an excess of amides, nitrogen will be withdrawn from the body; in absence of amides, a further amount of protein nitrogen would be necessary for the production of urine. The economising effect of amides is, it is suggested, to supply material for the kidneys, which can only work properly when producing urea.

The results would seem to indicate, further, that cows require no

nitrogen for maintenance. It is probable, however, that a small amount of nitrogen, a few grams per day, is necessary.

Notwithstanding the, sometimes considerable, amounts of nitrogen as nitrates supplied in the food, no trace of nitrates could ever be detected in the excrementitious matters. Experiments in which nitrates were added to the contents of the large intestine showed that in three days the whole of the nitrate was lost as free nitrogen and some of the original nitrogen as well. In the case of the small intestine, a considerable portion of nitrate was denitrified in a week.

N. H. J. M.

Temperature-coefficient of the Velocity of Nerve Conduction. CHARLES D. SNYDER (*Amer. J. Physiol.*, 1908, 22, 179—201).—The temperature-coefficient of the velocity of conduction in frog's sciatic nerves lies for the most part between 2 and 3.

Exceptions to this rule are assumed to be due to differences in the chemical time reaction of the conducting substances in the nerve. The meaning of the results is discussed at length, but the most important conclusion reached is that nerve conduction cannot be a purely physical phenomenon.

W. D. H.

The Partition of Lecithin in the Animal Organism. JOSEPH NERKING (*Biochem. Zeitsch.*, 1908, 10, 193—203).—The whole animal, or its organs, was passed through a sausage machine, extracted with hot alcohol, and then with chloroform or ether. The residue of the extract was incinerated, and, from the phosphoric acid in the ash, the amount of lecithin was calculated. In two rabbits, the total yield was 0.36% and 0.4% of the body-weight respectively. In a hedgehog, the percentage reached 0.8. In other cases, the individual organs were examined, and the results are given in tables. The large percentage of lecithin in the hedgehog was again noted, especially in bone marrow and suprarenals; this is possibly related to the comparative immunity against snake-bite this animal possesses.

W. D. H.

Influence of Salts and Non-electrolytes on the Heart. STANLEY R. BENEDICT (*Amer. J. Physiol.*, 1908, 22, 16—31).—Experiments on strips of the turtle's ventricle show that certain substances alter its irritability without inciting rhythmical contractions. The sodium chloride latent period represents the time necessary to reach a condition of tonus suited to rhythmic activity; it is not caused by lack of calcium ions or of oxygen. The sodium chloride arrest is attributed to loss of irritability and not to asphyxiation. Langendorff's hypothesis that the products of activity act as stimuli to rhythmic action is regarded as probable. Excess of oxygen and of diffusible calcium compounds do not increase favourable oxidation as Martin considers. The anion probably plays an active rôle in the action of salt solutions on heart tissue, but under certain conditions non-electrolytes (sugars) may induce a series of beats.

W. D. H.

The Extractives of Muscular Tissue. X. R. KRIMBERG (*Zeitsch. physiol. Chem.*, 1908, 55, 466—480).—The main result of these investigations is to show that the base discovered by Gulewitsch and Krimberg, and called by them carnitine, is identical with the base described by Kutscher under the name of novaine.

Meat-extract solution was treated with tannic acid, and the filtrate, after separation of tannic acid, &c., made alkaline with lead hydroxide and evaporated to a small bulk; crystals separated, and the mother liquor was then treated with silver nitrate and barium hydroxide. From the precipitate, a base was obtained, m. p. 239—240°, whereas, according to Gulewitsch, carnosine has m. p. 241—245°. This is apparently identical with Kutscher's ignotine.

From the filtrate from the silver nitrate and barium hydroxide precipitation, a mixture of bases was isolated by means of phosphotungstic acid and mercuric chloride precipitations. From this mixture, the oblitine was separated by taking advantage of the relatively small solubility of the platinichloride; the other bases were separated by fractional precipitation with gold chloride. The greater part consisted of a base agreeing in properties with carnitine and with the base described as novaine. In addition, small quantities of another base were obtained from the last fraction; the composition of this corresponded with the formula $C_6H_{14}O_2N_2$, but it was not identical with lysine.

S. B. S.

Formation of Lactic Acid and Carbon Dioxide in Muscle. P. W. LATHAM (*Bio Chem. J.*, 1908, 3, 193—206).—Theoretical views as to the way in which lactic acid and carbon dioxide may originate from the protein of muscle during the processes of contraction and rigor mortis.

W. D. H.

Chemical Investigations on the Teeth. TH. GASSMANN (*Zeitsch. physiol. Chem.*, 1908, 55, 455—465).—The inorganic constituents and loss on destruction of organic matter were estimated. The loss on ignition varied in the different kinds of teeth investigated between 18.33% and 25.99%; the calcium between 27.23% and 31.65%. The greater the former number the smaller the latter. No fluorine could be detected.

S. B. S.

The Cleavage Products of the Eggshell of Scyllium stellare. FRITZ PREGL (*Zeitsch. physiol. Chem.*, 1908, 56, 1—10).—One hundred parts of the dry and ash-free organic substance of the egg-shell of this dogfish yield glycine, 2.6; alanine, 3.2; leucine and isoleucine, 5.8; proline, 4.4; phenylalanine, 3.3; aspartic acid, 2.3; glutamic acid, 7.2; tyrosine, 10.6; lysine, 3.7; arginine, 3.2; histidine, 1.7; tryptophan, present, and cystine, questionable. These numbers are compared in a table with the results obtained from the shells of *Testudo graeca*, the *membrana testacea* of the hen's egg, with keratin, and with koilin. The figures are very different in each case; the high percentage of tyrosine in the present analysis is striking.

W. D. H.

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Elementary Analysis and Distribution of Nitrogen in Various Egg-shells. HANS BUCHTALA (*Zeitsch. physiol. Chem.*, 1908, 56, 11—17).—The following table contrasts the elementary composition of the egg-shells or membranes examined in the following animals:

	<i>Scyllium stellare.</i>	<i>Pristiurus melanostomus.</i>	<i>Scyllium canicula.</i>	<i>Scyllium catulus.</i>	Membrana testacea of hen.	<i>Coluber natrix.</i>
C	53.92	51.45	53.64	51.50	48.78	51.68
H	7.33	6.61	6.49	6.51	6.64	7.24
N	15.08	14.33	14.23	15.34	16.43	16.87
S	1.44	1.52	1.33	0.88	4.20	0

The following table gives the distribution of nitrogen (Hausmann's method); the figures not in brackets give the percentage of nitrogen in the material; those in brackets, the percentage in relation to total nitrogen:

	Ammonia N.	Melanin N.	Mono-amino N.	Di-amino N.
<i>Scyllium stellare</i>	0.7 (5.09)	0.03 (0.56)	10.96 (79.68)	2.17 (15.8)
<i>Pristiurus mel.</i>	0.75 (5.13)	0.02 (0.14)	9.70 (66.45)	4.2 (28.8)
<i>Scyllium canic.</i>	0.64 (4.49)	0.04 (0.24)	9.21 (64.19)	4.4 (30.75)
Memb. testacea	0.89 (6.6)	0.03 (0.21)	9.81 (72.7)	2.77 (20.5)

W. D. H.

The Relations between Lipoid Liquefaction and Cytolysis. ERICH VON KNAFFL-LENZ (*Pflüger's Archiv*, 1908, 123, 279—293).—The experiments were carried out with sea-urchin eggs (*Strongylocentrotus purpuratus*). They were placed in sea-water to which had been added various substances, such as the ordinary organic solvents, fatty acids, chloral hydrate, bile salts, &c., and then re-immersed in ordinary sea-water and examined under the microscope to determine whether fertilisation, membrane formation, or cytolysis had taken place. The results obtained lead to the conclusion that the essential constituent of a cell-membrane is not a substance of a fatty nature; that the protoplasm is rich in lipoids, and is an emulsion of these substances with proteins; that physical and chemical treatment of the egg, which causes liquefaction of lipoids, causes also cytolysis; that the egg-protein can swell or be dissolved only after a change in the state of aggregation of the fats, and that cytolysis is brought about by the liquefaction of the lipoid and subsequent imbibition of water by, or solution of, the protein. All reagents which can liquefy the lipoids and cause cytolysis of the egg can, by short action and suitable concentration, lead to the formation of membranes (fertilisation membranes). The results thus confirm Loeb's hypothesis that membrane formation is due to lipoid liquefaction. S. B. S.

Excess of Chlorides in Lymph. ANTON J. CARLSON, J. R. GREER, and A. B. LUCKMARDT (*Amer. J. Physiol.*, 1908, 22, 91—103).—Lymph contains more chlorides than serum; the osmotic pressure of the neck lymph of the dog is higher than that of the serum, but anaesthesia produced by ether or by chloroform reverses this osmotic relation. The excess of chlorides is more than sufficient to account for the difference, and it renders filtration and transudation theories of lymph-formation untenable. The explanation of the excess is to be sought in the

relation of the lymph to the tissues rather than in the relation of the lymph to the blood. W. D. H.

Lymphagogue Action of Lymph. ANTON J. CARLSON, J. R. GREER, and F. C. BECHT (*Amer. J. Physiol.*, 1908, 22, 104--115).—Injection of lymph intravenously increases the flow of lymph from the thoracic duct. There is also an increase from the neck lymphatics, but the experimental evidence of this is not so clear. Among the views advanced to explain this, the hypothesis is put forward that a lymph-forming hormone is produced in the tissues. The formation of lymphatic lymph and tissue lymph do not always run parallel; thus activity of the salivary glands and pancreas do not always increase the lymph flow from those organs. W. D. H.

Comparative Investigations on the Elimination of Iodine after Administration of Potassium Iodide and Saiodin. EMIL ABDERHALDEN and KARL KAUTZSCH (*Chem. Zentr.*, 1908, i, 874; from *Zeitsch. exper. Path. Ther.*, 1907, 4, 716--719. Compare Basch, this vol., ii, 521).—Saiodin [the calcium salt of iodobenenic acid, $(C_{22}H_{42}O_2I)_2Ca$] does not undergo scission after treatment either with steapsin, gastric juice, or pancreatic and gastric juices. After administration of the drug, alkali iodides were sought for in the faeces to determine whether such substances had been excreted by the intestine. They were not found, but the iodine, after full absorption of the saiodin, can be detected in the urine. The rate of excretion, however, is very much retarded when compared with that which follows the administration of potassium iodide. S. B. S.

Excretion of Bromides by the Kidney. WORTH HALE and CASRIEL FISHMAN (*Amer. J. Physiol.*, 1908, 22, 32--42).—After a single dose, the excretion of bromides is much delayed, but the delay is less after successive doses. Iodides are excreted more rapidly. The excretion of calcium bromide and sodium bromide occurs at the same rate. The amount of diuresis holds no absolute relation to the amount of bromide excreted. The observations were made on man. W. D. H.

The Elimination of Alanine by the Urine. THEODOR BRUGSCH and RAHEL HIRSCH (*Chem. Zentr.*, 1908, i, 874; from *Zeitsch. exper. Path. Ther.*, 1907, 4, 947--948).—The authors maintain the correctness of their statement, despite Oppenheimer's adverse criticism (*Abstr.*, 1907, ii, 900), that the assimilation limits of *dl*-alanine during starvation are far below the normal. S. B. S.

The Elimination of Conjugated Glycuronic Acid in the Bile. MANFRED BIAL (*Chem. Zentr.*, 1908, i, 1076; from *Zentr. Physiol.*, 1908, 21, 751--756).—The separation of conjugated glycuronates by means of the bile constitutes a specific secretion, and, under certain conditions, considerable quantities of paired glycuronates are eliminated in this way instead of by the urine. S. B. S.

Origin of Uric Acid and its Relation to Digestion. THEODOR BRUGSCH and ALFRED SCHITTENHELM (*Chem. Zentr.*, 1908, i, 873; from *Zeitsch. exper. Path. Ther.*, 1907, 4, 761--768).—The authors

controvert Hirschstein's view (*Arch. exp. Path. Pharm.*, 1907, 57, 229), according to which at least 70% of the uric acid excreted is due to digestion processes, and therefore appears in the urine after a purine-free diet. They hold rather that the principal part of the uric acid and purine compounds is due to destruction in the organism resulting from the ordinary processes of life.

S. B. S.

Glycogen in Mouse Tumours. M. HAALAND (*J. Path. Bact.*, 1908, 12, 439).—There was found to be no relation between the amount of glycogen and the rate of growth in mouse tumours as was stated to be the case by Brault.

W. D. H.

Influence of Cold and Exercise on Sugar Excretion in Phloridzin Glycosuria. GRAHAM LUSK (*Amer. J. Physiol.*, 1908, 22, 163—173).—Lüthje states that in pancreatic diabetes, external cold raises the excretion of sugar; this conclusion is doubtful, and has been criticised previously by others. In phloridzin glycosuria, the dextrose: nitrogen ratio is unchanged by feeding on fat, by the application of cold, or by mechanical work. All this proves that sugar is derived from protein and not from fat. Mistatements regarding the magnitude of the dextrose: nitrogen ratio made by others are corrected.

W. D. H.

Production of Sugar from Glutamic Acid Ingested in Phloridzin Glycosuria. GRAHAM LUSK (*Amer. J. Physiol.*, 1908, 22, 174—178).—Subcutaneous injection of glutamic acid in phloridzin glycosuria (in a dog) raises the output of sugar. The results, which are stated in the form of tables, support the author's previously expressed views on carbohydrate metabolism.

W. D. H.

Effect of Potassium Iodide on Ptyalin. C. H. NEILSON and O. P. TERRY (*Amer. J. Physiol.*, 1908, 22, 43—47).—The addition of small quantities of potassium iodide to saliva increases the amount of maltose formed. When the drug is given by the mouth and the saliva collected, the secretion has its amylolytic power increased, except in a few patients in whom, for some reason, no potassium iodide appeared in the saliva.

W. D. H.

Action of Lactic Acid on the Isolated and Surviving Heart of Mammals. E. LOUIS BACKMAN (*Chem. Zentr.*, 1908, i, 1076; from *Skand. Arch. Physiol.*, 1908, 20, 162—196).—The action was investigated by means of the method of Laugendorff and Locke with Göthlin's solution (0.63% NaCl, 0.025% CaCl_2 , 0.05% KCl, and 30% NaHCO_3) as perfusion medium. In addition to a general vasodilatation, two special actions were noticed, namely, a muscular paralysis with low concentration, and a stimulating action on the motor ganglia of the heart with more concentrated solutions (0.25—0.5% solutions); they confirm Rauke's hypothesis that lactic acid is a cause of peripheral fatigue.

S. B. S.

Action of Digitalis and Strophanthus on the Circulation. CARL TIGERSTEDT (*Chem. Zentr.*, 1908, i, 1077; from *Skand. Arch. Physiol.*, 1908, 20, 115—167).—Measurements of blood pressure and

volume lead to the conclusion that the increased pressure produced by digitalis and strophanthus is mainly due to contraction of the vessels. No distinct difference could be detected between the behaviour of digitalis and strophanthus.

S. B. S.

The Behaviour of Salicin in the Normal and Diabetic Organism. KAORU OMI (*Biochem. Zeitsch.*, 1908, 10, 258—263).—The alimentary canal contains no ferments which act on salicin, but the liver and kidney of herbivora (rabbit, sheep, ox, pig) contain an emulsin which can be demonstrated by the use of extracts of those organs. In carnivora and man, this action is either slight or absent. In dogs, however, after extirpation of the pancreas, the emulsin action occurs in liver extracts.

W. D. H.

Excretion of Ethereal Sulphates after giving Salicin to Normal and Diabetic Dogs. CHIASABURO KUSUMOTO (*Biochem. Zeitsch.*, 1908, 10, 264—274).—In herbivora (rabbits), the administration of salicin by the mouth or under the skin causes the excretion of salicylic acid and an increase in the ethereal sulphates of the urine. In normal dogs, this is more marked, especially when the drug is given by the mouth. At least 10% of the amount given is acted on by the emulsin of the tissues. In dogs deprived of the pancreas, this is usually increased.

W. D. H.

Atoxyl and Aniline Poisoning. FERDINAND BLUMENTHAL and FRIEDRICH HERSCHMANN (*Biochem. Zeitsch.*, 1908, 10, 240—244).—The toxic effects of atoxyl have been attributed by some to arsenic and by others to aniline poisoning. The latter view is rendered unlikely by the discovery that neither aniline nor *p*-aminophenol-sulphonic acid can be detected in the urine after administration of atoxyl. The drug is apparently excreted in the form of a closely-allied derivative still containing both arsenic and the amino-group.

G. B.

Chemistry of Vegetable Physiology and Agriculture.

Reservoir for Storing Aseptic Liquids. LOUIS GAUCHER (*Ann. Chim. anal.*, 1908, 13, 212—214).—The reservoir (flask, or Wolff's bottle, with a syphon) is made entirely of glass without corks, and is so arranged that no air can enter without first having been filtered through a layer of cotton-wool. For details of construction, the illustrations in the original should be consulted.

L. DE K.

Behaviour of Algæ to Salts at Certain Concentrations. T. TAKEUCHI (*Bull. Coll. Agr. Tōkyō*, 1908, 7, 623—629).—Solutions of potassium nitrate, chloride and sulphate, mono- and di-potassium

phosphate, the corresponding salts of sodium, and calcium chloride and nitrate were employed in equal molecular and equivalent concentrations, the standard solution being a 1/10 gram-mol. solution of potassium nitrate. Threads of *Spirogyra nitida* were kept in the solutions at 8—20°.

Potassium nitrate (1.01%) killed all the cells in eight days. In the corresponding calcium nitrate solution, the cells remained healthy much longer, and even in 2.46% solutions most cells seemed normal after two weeks.

Taken altogether, the results show that calcium salts, at moderate concentrations, are less injurious than equivalent amounts of sodium and potassium salts. The injurious action of magnesium salts can only be completely overcome by calcium and not by sodium or potassium salts.

N. H. J. M.

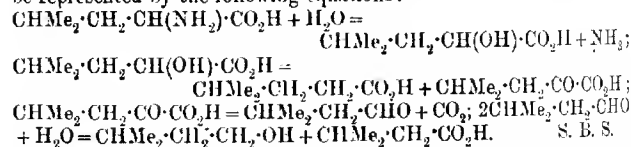
Galvanotropism in Bacteria. JAMES FRANCIS ABBOTT and ANDREW CREAMORE LIFE (*Amer. J. Physiol.*, 1908, 22, 202—206).—*Teramo*, *subtilis*, and typhus bacilli in a neutral medium form definite gatherings at the cathode, an extremely weak current being used. If grown in acid media, this response is intensified. In alkaline media, they gather at the anode. Bacteria killed by heat show no response.

W. D. H.

The Decomposition of Amino-acids by *Bacillus proteus vulgaris*. PAUL NAWIASKY (*Arch. Hygiene*, 1908, 66, 209—243).—The decomposition products obtained by the action of *B. proteus vulgaris* on various amino-acids were investigated, and in certain cases determined quantitatively. Not all amino-acids are readily attacked by the bacillus. The following acids, which were investigated, are arranged in order according to the readiness with which they are attacked, the most easily decomposable being placed first; aspartic acid, leucine, aminovaleric acid, phenylalanine, tyrosine, arginine, creatine, glycine, alanine. In the cases of *L*-proline and glutamic acid, the decomposition is due entirely to respiration.

Asparagine is readily decomposed into succinic and acetic acids, ammonia, and carbon dioxide. This decomposition can also be brought about by dead bacteria, although slowly and incompletely; the rate of decomposition is proportional to the acting mass of the bacteria.

Aminovaleric acid yields as a decomposition product, butyric acid, and leucine yields amyl alcohol. The decomposition of the latter may be represented by the following equations:



S. B. S.

Nitrification in Black Soils. Influence of Different Factors on Nitrification and the Amounts of Nitrates in the Soil at Different Times of the Year. W. SASANOFF (*J. exper. Landw.*, 1907, 8, 35—38).—Whilst the black soils of Russia are greatly

benefited by superphosphate, sodium nitrate is only required in very small quantities. It is shown that in the Spring the soil may contain very small amounts of nitrates; in such cases, applications of 8 to 30 kilos. of sodium nitrate, not sown broadcast, but drill-sown below the seed, enable the plants to make a start. Later on, nitrification is sufficiently rapid for the requirements of the crop.

In order to promote the accumulation of nitrates in the soil, it is shown that suitable tillage, at the proper time, is of great importance. Farmyard manure was found to be of little, if any, use, whilst undecomposed organic matter, such as straw, hindered nitrification at first. Green manuring with leguminous and other crops has no appreciable effect on nitrification, and has the disadvantage that the growing crop disperses the moisture of the soil and takes up the nitrates.

N. H. J. M.

Inoculation Experiments with Azotobacter. JACOB C. LIPMAN and PERCY E. BROWN (28th Ann. Rep. New Jersey State Agric. Exper. Stat., 1906—1907, 141—170).—Successive gramineous crops (oats, maize, rye, maize, rye, and maize) were grown in sixty large cylinders containing sandy loam both without manure and with calcium carbonate, basic slag, farmyard manure, calcium carbonate + farmyard manure, and the same as the last with basic slag in addition. One series was without inoculation, and the others with *Azotobacter Vinelandii* and *A. Beijerinckii* respectively. The soils were manured and inoculated the first time about a year before the first seeds were sown, and the inoculation was repeated later on. The rye crops (green) were dug in each time.

The results obtained with the first crop showed on the whole greater yields of dry matter and nitrogen without than with inoculation. An examination of the soil then showed that, whilst *Azotobacter Beijerinckii* was abundant and vigorous in the pots manured with calcium carbonate and dung, most of the bacteria had either become feeble or failed altogether in the other pots. The soil conditions would seem to be more unfavourable for *A. Vinelandii*, which is much less abundant than *A. Beijerinckii* in the soils of New Brunswick (N. J.), than for *A. Beijerinckii*. The second crop (maize) gave somewhat similar results as the first, whilst the third crop (rye) gave greater yields in the inoculated than in the uninoculated pots. Taking the whole series, however, the final results showed no benefit from inoculation, whilst, as regards the soils themselves, there was sometimes a gain and sometimes a loss of nitrogen irrespective of inoculation.

Treatment with carbon disulphide before the fifth crop had no immediate uniform effect, but it seemed to benefit the sixth crop.

N. H. J. M.

Formation and Disappearance of Acetaldehyde under the Influence of Yeasts. AUGUSTE TRILLAT and SAUTON (*Compt. rend.*, 1908, 146, 996—999).—When baker's pressed yeast is vigorously stirred with dilute alcohol for several hours with free access of oxygen, acetaldehyde can be separated by distillation (1—2.5% of the alcohol employed). The action is primarily a vital one. At the

same time, acetaldehyde disappears fairly rapidly when added to yeast in dilute alcohol. G. B.

Effect of Temperature on the Respiration of Apples. FRED. W. MORSE (*J. Amer. Chem. Soc.*, 1908, 30, 876—881).—Apples undergo chemical changes twice or three times as fast with a rise of temperature of 10° between 0° and 20°. Respiration and, consequently, destruction of cell tissues goes on at low temperatures, and the keeping quality of apples is therefore limited even in cold storage.

N. H. J. M.

The Liberation of Carbon Dioxide by Dead Parts of Plants. A. J. NABOKICH (*Ber. deut. bot. Ges.*, 1908, 26a, 324—332).—In a high vacuum, seeds, seedlings, and various other plant objects gradually give off, after death, not inconsiderable quantities of carbon dioxide. This liberation of carbon dioxide is independent of ferments or bacteria, and also of the manner in which the plant has been killed (whether by freezing, heating, boiling acids, or superheated steam).

Aerobic cultures of fungi set free ammonia, which is retained by the carbon dioxide of respiration as ammonium carbonate, and is slowly set free in anaerobic life by the organic acids formed under such conditions; this slow liberation of carbon dioxide simulates intramolecular respiration. G. B.

Influence of Didymium [and Glucinum] on Plants. C. KANOMATA (*Bull. Coll. Agr. Tokyo*, 1908, 7, 637—640).—Barley was grown in pots containing 10 kilograms of loamy soil, manured with minerals and potassium nitrate. Three pots received, in addition, 0.01, 0.1, and 0.5 gram of "didymium" nitrate (the unseparated salts of praseodymium and neodymium) previously neutralised with sodium hydroxide. The plants grown with 0.01 gram of "didymium" nitrate showed a considerable increase in total weight (17.5%), and in the weight (42.4%) and number of ears, as compared with the control pot, whilst the larger applications diminished the yield. A similar stimulating effect was observed when neutralised "didymium" nitrate was applied to mustard, *Raphanus sativus radicola*, and tobacco at the rate of 1 per million of soil.

The increase in the three last experiments amounted to 13.7% with mustard, 27.0% with *Raphanus*, and 32.1% with tobacco.

Glucinum nitrate neutralised with sodium hydroxide, when applied to oats at the rate of 10 per million of soil, had no decided effect (the yield of fresh substance was 4.5% higher than in the control pot), whilst larger amounts (100 and 500 per million) reduced the yield.

N. H. J. M.

Oxydases in India-rubber. DAVID SPENCE (*Bio.-Chem. J.*, 1908, 3, 165—181).—The observations recorded show that the darkening of raw rubber is due to an oxydase associated with the protein or so-called insoluble constituent of the rubber. Whether it is responsible for other changes which occur on keeping (decomposition, &c.) further

work will determine. The ferment is probably reversible in its action, and it is suggested that the function of caoutchouc in the latex is not merely protective to the plant, and that the latex does not merely serve as a reserve store for water; caoutchouc itself is probably a reserve food-stuff for the plant.

W. D. H.

Toxic Substance Excreted by the Roots of Plants. F. FLETCHER (*Mem. Dept. Agric. India; Bot. Ser.*, 1908, 2, No. 3).—Plot experiments were made in which sorghum, cajanus, cotton, and sesamum were grown next to each of the others and next to fallow. Taking the yield of the outside rows next to fallow as 100, the differences in the middle rows of each plot and of the outside rows next to the plots bearing the other crops are assumed to indicate depression of yield due to a toxic substance secreted by its own roots and by the roots of the other plants. A further experiment is described in which cotton and sorghum were grown in alternate rows two feet apart. The results show great regularity, and the conclusions are drawn (1) that all plants excrete a substance which is toxic to themselves and to other plants; (2) that different crops excrete varying amounts of the substance, and (3) that the sensitiveness of different crops to the same amount of the poison varies.

Water culture experiments were made with the above plants and with wheat and grain in addition, each plant being grown in water previously used for the same plant and for each of the others. Grain water was found to be the most toxic, then sesamum, wheat, cotton, cajanus, and sorghum water. The strength of the solution is, of course, arbitrary; the regularity of the results indicates, however, that the toxic substance is the same in all plants.

As regards the amount of toxic substance produced, the solution in which ten cotton plants (weighing 0.4 gram when air dry) were grown gave with potassium sulphate a precipitate weighing, when dry, 0.21 gram. The substance seems to be an alkaloid (the base itself, not a salt) which differs from the commoner alkaloids in being sparingly soluble. Its toxic effect is corrected by tannic acid, and it is usual to manure spice gardens and rice fields with leaves containing tannic acid.

N. H. J. M.

Composition of Rice Straw. T. TAKEUCHI (*Bull. Coll. Agr. Tôkyô*, 1908, 7, 619—621).—Analysis of two samples of straw (1) from a favourable harvest and (2) from a poor harvest give the following results:

Dry matter.	N.	Crude fat.	Crude fibre.	Dextrose.	Sucrose.	Starch, hemi-celluloses.	Pentosans.	Crude ash.	SiO ₂ .
1. 87.69	0.67	1.36	31.16	2.25	0.79	14.86	14.28	11.42	5.39
2. 90.15	1.48	1.65	28.72	3.28	0.96	18.75	16.55	12.35	6.13

N. H. J. M.

Continuous Growth of Peas on the Same Soil. SHIGEHIRO SUZUKI (*Bull. Coll. Agr. Tôkyô*, 1903, 7, 575—577).—Experiments with peas grown for four years in succession in the same humous loam

with mineral and nitrogenous manures failed to give any indications of pea-sickness. The yield tended rather to increase. Very few nodules were found on the roots of the plants.

Heating the soil in steam at 100° for four hours on three consecutive days had practically no effect on the yield.

The conclusion is drawn that pea- and clover-sickness may be sometimes due to deficiency of phosphoric acid in the soil, and some times to want of potash, as suggested by Gedroiz (*J. exper. Landw.*, 1908, 8, 61).
N. H. J. M.

Behaviour of Onions to Stimulants. I. NAMBA (*Bull. Coll. Agr. Tôkyô*, 1908, 7, 635—636).—Addition of 0.1 gram of manganese sulphate to 8 kilograms of soil, corresponding with 22 kilos. per hectare, increased the yield of onions (leaves, bulbs, and roots) 59.2% whilst 0.2 gram gave an increase of 34.2%.

Sodium fluoride applied at the rate of 2.2 kilos. per hectare (0.01 gram in 8 kilos. of soil) increased the yield 80.2%. With 0.05 and 0.2 gram, the increase was reduced to 31.5 and 7.8% respectively.
N. H. J. M.

Cultivation of Sugar-Beet. Potassium Manuring of Beet Soils. E. SAILLARD (*Bied. Zentr.*, 1908, 37, 426—427; from *J. d'Agric. Prat.*, 1907, i, 454).—Determinations of sugar, potassium, and sodium in sugar-beet from all parts of France where they are grown showed that with diminished percentages of sugar there is a regular increase in the sodium expressed as percentage in the portion of the a-l soluble in hydrochloric acid. The potassium was found to vary very slightly. Roots containing 16—17% of sugar contained 3.6% K_2O and 5% Na_2O in the ash (excluding insoluble portion), whilst roots with 8—11% of sugar contained 38% K_2O and 17.5% Na_2O in the ash. The paralysing action of sodium is shown by results obtained near the sea, where it is impossible to grow roots with high percentages of sugar. In manuring sugar-beet, sodium nitrate should be employed in moderation. The following manures are recommended: superphosphate, 300—500 kilos.; potassium (as sulphate, chloride, or kainite), 75—90 kilos.; nitrogen (as sodium nitrate), 25—40 kilos. per hectare, and the rest of the nitrogen in an organic form, as farmyard manure.
N. H. J. M.

Experiments with Different Varieties and on the Storage of Mangolds. BOUWE SJOELENA and C. K. VAN DAALEN (*Verslagen Landbouwkund. Onderzoek Rijkslandbouwproefstat.*, 1907, No 2; 31—49. Compare Miller, *Abstr.*, 1900, ii, 430; *J. Roy. Agric. Soc.*, 1902, 63, 135).—Experiments were made with fourteen varieties of mangolds, manured with superphosphate only and grown in rows 50 cm. apart, the distances in the rows being 40 and 50 cm. respectively. Determinations of total weight, dry matter, and sugar were made in October, when the crop was taken up, and also in the clamped roots in January and in April.

The weight of the roots was greatest, as well as the average yield of sugar, in the case of the roots grown 40 cm. apart.

In January the average loss in weight was 2%, and in the case of the varieties containing the lower percentages of sugar, about 1.5% of sucrose was converted into reducing sugar. Inversion was slower in the case of the roots containing high amounts of sugar.

In April there was a further loss of about 1% in the weight of the roots, and the amount of reducing sugar increased to 2—3%, although in some cases it remained below 1%.

The average loss of dry matter from October to April was 9.35%; the greatest loss was 20.6%, and in two cases there was a slight gain. The loss of sugar amounted in some cases to more than 10%.

N. H. J. M.

Manurial Experiments on Mangolds with Calcium Cyanamide and Sodium Nitrate. S. KIRPPEL (*Bied. Zentr.*, 1908, 37, 386—391; from *Fühling's Landw. Zeit.*, 1907, 56, 535).—Field experiments with six varieties of mangolds resulted, in each case, in higher yields of dry matter and sugar when manured with calcium cyanamide than with sodium nitrate. The results are partly attributed to frequent rain and consequent washing of sodium nitrate into the subsoil.

N. H. J. M.

Occurrence of Cyanogenetic Glucosides in Feeding-stuffs. THOMAS A. HENRY and SAMUEL J. M. AULD (*J. Soc. Chem. Ind.*, 1908, 27, 428—433).—Since it has been found that many plants which are used as feeding-stuffs contain cyanogenetic glucosides (Dunstan and Henry, *Abstr.*, 1901, i, 39, 647; 1902, ii, 578; 1904, ii, 71; 1907, i, 1063; 1907, ii, 983; Dunstan, Henry, and Auld, *Abstr.*, 1906, ii, 794, 795; 1907, ii, 572), it has been considered desirable to record the amounts of hydrogen cyanide yielded under different conditions and to describe the methods employed in their estimation. In addition to giving this information, the present paper introduces certain new facts.

It has been found that when these plants are ground and macerated with water, the amount of hydrogen cyanide developed does not correspond with the quantity which would be produced by the total decomposition of the glucoside present. This is due to the inhibiting action exerted by the dextrose produced during the hydrolysis.

Two samples of linseed cake which were examined furnished 0.032 and 0.045% of hydrogen cyanide. It has been observed that some white varieties of the seeds of *Phaseolus lunatus* yield hydrogen cyanide. Traces were obtained from certain French haricots, from 0.026 to 0.068% from some Ceylon varieties, and 0.002% from "butter beans." In the case of the bitter cassava, the green branches did not yield any hydrogen cyanide, the stem furnished 0.007%, and the whole tubers, 0.013%. The stem of the sweet cassava gave 0.005%, the whole tubers, 0.014%, the rind of the tubers, 0.040%, and the inner portion, 0.007%.

E. G.

Effects of Feeding with Maize. Certain Properties of Zein. I. SILVESTRO BAGLIONI (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 609—617).—The author discusses the work of Paladino-Blandini

(*Arch. farm. sper. ecc.*, 1907, 6, 57), Bezzola (*Zeitsch. Hygiene*, 1907, 56, 75), Scheunert and Grimmer (Abstr., 1906, ii, 239), and Szumowski (Abstr., 1902, ii, 674) on zein or maize as a food-stuff, and on its action in causing the disease termed pellagra.

Zein yields relatively large proportions of phenylalanine and tyrosine when decomposed, and free phenolic compounds can often be detected in maize which has been attacked by moulds or other micro-organisms. If zein, suspended in water, is treated with potassium hydroxide and copper sulphate solutions, the violet biuret coloration only appears after a few minutes; if, however, the zein is first treated for a short time with potassium hydroxide solution, it yields the coloration immediately the copper sulphate solution is added. The delay in the appearance of the reaction is occasioned by the insoluble zein requiring to be degraded into simpler proteoses by the action of the potassium hydroxide (compare Dennstedt and Hassler, Abstr., 1906, i, 916).

The digestion of zein by infusions of the pancreas or intestinal mucus of the dog or hog, or by commercial pepsin preparations, proceeds slowly and with difficulty. In no case did the zein undergo complete solution, possibly owing to the accumulation of the products of digestion, and to the weakening of enzymatic activity. Experiments on the digestion of zein by means of extracts of germinating maize corns have not, as yet, met with success.

Guinea-pigs fed on a paste of maize or wheat flour and water exhibit all the symptoms of general decline, and die in a period varying from a few days to a month. If part or all of the maize or wheat flour is replaced by zein, the animals exhibit symptoms of poisoning somewhat similar to those observed in cases of phenolic intoxication.

T. H. P.

New Apparatus for Showing the Ammonia-condensation Power of Soils. GEORG RÖSING (*Chem. Zentr.*, 1908, i, 1323; from *Zeitsch. landw. Vers.-Wesen Oesterr.*, 1908, 11, 133—127).—A modification of the apparatus described by Wohltmann and Schneider (Abstr., 1905, ii, 649), whereby the volume of the gas before and after the adsorption may be arrived at, and thus the calculation of the amount by weight rendered possible.

J. V. E.

Physical and Chemical Processes in the Production of Soils. PAUL RÖHLAND (*Biol. Zentr.*, 1908, 37, 289—291; from *Landw. Jahrb.*, 1907, 36, 473).—The diffusion of water and plant nutrients in soils is intimately connected with the presence of colloids, mainly silicic acid and aluminium hydroxide, produced by the interaction of felspar, water, and carbon dioxide. As regards chemical actions, the replacement of basic constituents in double silicates by bases dissolved in the soil water is of great importance, as, for instance, when sodium applied in a manure liberates potassium from insoluble compounds present in the soil.

The processes of adsorption depend on the different concentration of those portions of the soil water which are in contact with the surface of substances such as double silicates, clay, humus, and ferric

hydroxide, &c., the more complex substances, such as phosphates, being more readily adsorbed than simpler compounds like potassium chloride. Another factor of importance is the mutual action of salts on solubility. The solubility of calcium sulphate, for instance, is increased in presence of sodium, potassium, and ammonium salts, and more by sodium nitrate than by sodium chloride, so that the availability of superphosphate, in which the particles of phosphates are encased in calcium sulphate, is increased by the presence of the above-mentioned salts.

N. H. J. M.

Why are Poor Sandy Soils Often Easily Injured by Liming? H. YOKOYAMA (*Bull. Coll. Agr. Tōkyō*, 1908, 7, 615—617).—Experiments with oats grown in purified quartz sand manured with ammonium nitrate, potassium sulphate, sodium phosphate, and different amounts of limestone and magnesite showed that further addition of lime to sand poor in lime caused a greater depression in yield than in the case of sand rich in lime, and that the ratio $\text{CaO}:\text{MgO}=5:1$ is less favourable than the ratio $1.8:1$. The conclusion is drawn that injury to sandy soils by liming is not due to destruction of bacteria or to lessened assimilability of the phosphoric acid (except when bone-dust or phosphorite are present), but to an unsuitable lime-magnesia ratio. Dolomitic limestone should be employed.

N. H. J. M.

Changes of Availability of Nitrogen in Soils. OSCAR LOEW and KEIJIRO ASO (*Bull. Coll. Agr. Tōkyō*, 1908, 7, 567—574).—A culture solution containing mineral nutrients and glycerol, inoculated with *Bacillus mycoides*, to which peptone and sodium carbonate were added subsequently, gradually developed films, which were distributed through the liquid by shaking. After six weeks, the contents of two flasks which no longer produced films were evaporated down in a vacuum. A gram of soil was added to one portion of the solution, whilst a second portion was boiled for a few minutes before addition of soil. The solution which had been boiled soon developed a luxuriant film of microbes, whilst the solution which had not been boiled remained unchanged for four weeks. The results show that soil bacteria can produce a bacteriolytic enzyme which renders new bacterial growth difficult, and furnishes some explanation why bacterial life does not increase infinitely in organically manured soils.

Gerlach and Vogel's observation that *Azotobacter* requires calcium was confirmed. In culture solutions containing mannitol and sodium malate respectively, growth failed until small amounts of calcium chloride were added (compare Christensen, this vol., ii, 67).

As regards the chemical process of nitrogen fixation, it is suggested that nitrogen combines with the elements of water, producing ammonium nitrite, the nitrous acid being at once reduced to ammonia. Nitrous acid has been detected in leguminous root nodules. The view that nitrous acid may be produced by oxidation is supported by results obtained by platinum black and alkali (compare Loew, *Abstr.*, 1890, 1051, and Wöhler, *Abstr.*, 1904, ii, 44).

N. H. J. M.

Ammonia-soluble Phosphoric Acid of the Soil. GEORGE S. FRAPS (*Amer. Chem. J.*, 1908, 39, 579—586).—In the course of an investigation on the phosphoric acid of the soil, a study has been made of the phosphoric acid which is extracted by ammonia from a soil which has been previously treated with hydrochloric acid. It has been found that the phosphoric acid so dissolved is partly in organic and partly in inorganic combination, and should therefore not be regarded as being entirely of the nature of "humus-phosphoric acid."

E. G.

Pot Culture Experiments, 1906-7. JOHN A. VOELCKER (*J. Roy. Agric. Soc.*, 1907, 68, 264—266. Compare Abstr., 1905, ii, 754; 1906, ii, 888).—Lithium chloride or sulphate, in very small quantities (0.05 gram Li to 100 of soil) reduced the yield of wheat to 25%, the action being largely due to the stunting of root growth.

Iron sulphate, in similar amount, increased the produce materially, whilst manganese chloride and sulphate, not exceeding 1 cwt. per acre, are also beneficial.

The greater benefit observed in field experiments by the ploughing in of mustard as compared with vetches is shown by experiments in pots to be due to physical conditions of the soil, the vetches producing a light and open condition resulting in a much greater loss of water than is the case with mustard.

Experiments on the application of different amounts of lime and magnesia to soil growing wheat and barley showed that as the lime and magnesia ratio approaches 1:1, the wheat grain tends to show greater strength. When the relation of MgO:CaO is increased, the roots become abnormally extensive and fibrous.

With regard to the acid condition produced in Stackyard Fields by the continued application of ammonium salts to a soil deficient in lime, it is shown that the failure of the crop is due to the presence of a poisonous substance soluble in water, or to the growth of some lower forms of vegetation.

N. H. J. M.

Manurial Experiments with Sodium Nitrate, Ammonium Salts, and Calcium Cyanamide. PAUL WAGNER, G. HAMANN, and A. MÜNZINGER (*Bied. Zentr.*, 1908, 37, 366—386; from *Arb. deut. landw.-Ges.*, 1907, No. 129. Compare *ibid.*, No. 80).—The results of experiments with cereals showed that manuring with ammonium salts produced 77% of the amount of grain obtained with corresponding amounts of sodium nitrate, and that 63% and 46% of the nitrogen applied as nitrate and as ammonium salts respectively was recovered. In the case of sugar-beet and mangolds, the amounts of nitrogen recovered were 63% and 43%.

The lower results obtained with ammonium salts as compared with nitrate are attributed to loss as ammonia, and to fixation, both chemical and physical, of some of the ammonia by zeolites. Clay soils retain appreciable amounts of ammonia even after distillation with magnesia. It is suggested that ammonia fixed in this manner escapes nitrification.

Calcium cyanamide has no injurious effect when applied immediately

before sowing the seed if employed in normal amounts and evenly distributed; its effect is, however, sometimes increased by applying a week or two before sowing. Soils very rich in humus or deficient in lime should be limed before using calcium cyanamide. Experiments with oats, winter rye, and barley showed that the amounts of nitrogen as cyanamide utilised were 83, 87, and 69 respectively compared with sodium nitrate = 100. In the case of mangolds, the result was less satisfactory, the amount of nitrogen recovered being 56% as compared with sodium nitrate.

N. H. J. M.

Manurial Experiments with Calcium Cyanamide. ALBERT STUTZER (*Bied. Zentr.*, 1908, 37, 422—423; from *Ill. landw. Zeit.*, 1907, 27, No. 78).—Field experiments, under very unfavourable climatic conditions, on a raw, sandy loam in which oats and barley were manured with ammonium salts, calcium cyanamide ("stickstoffkalk"), and sodium nitrate respectively, in addition to soluble phosphoric acid (50 kilos.) and potash (100 kilos. per hectare). Sodium nitrate gave the highest results, whilst calcium cyanamide gave, on the average, 84.5% of the grain obtained with nitrate. The results obtained with ammonium salts were very variable.

N. H. J. M.

Efficacy of Calcium Cyanamide under Different Manuring Conditions. I. NAMBA and C. KANOMATA (*Bull. Coll. Agr. Tōkyō*, 1908, 7, 631—634).—In pot experiments with oats and onions, it was found that rather higher yields were obtained when calcium cyanamide was employed in conjunction with double superphosphate than with disodium phosphate. Similar results were obtained by Inamura (*Abstr.*, 1906, ii, 891) with *Brassica chinensis*.

Further experiments with *Brassica chinensis* and oats, in which bone-dust was used in conjunction with ammonium sulphate and calcium cyanamide respectively, showed that the latter had no depressing effect on the availability of the bone-dust.

N. H. J. M.

Action of "Kalkstickstoff," "Stickstoffkalk," and Calcium Nitrate. BOUWE SROLLEMA and J. C. DE RUYTER DE WILDT (*Verslagen Landbouwkund. Onderzoek. Rijkslandbouwproufstad*, 1907, No. 2).—Calcium cyanamide reacts with water, forming calcium hydroxide and the compound $\text{Ca}(\text{N}:\text{C}:\text{NH})_2$, the latter being gradually decomposed by calcium hydroxide and cyanamide into the basic salt, $\text{C}(\text{N}:\text{CaOH})_2$, which slowly polymerises to dicyanodiamide.

It is shown that the injurious action of calcium cyanamide on germination is not due to lime as stated by Immendorf and Thielebein (*Fühling's Landw. Zeit.*, 1905, 54, 792), or to the gases produced from calcium carbide and phosphide or to dicyanodiamide, but that it is due to the basic salt already mentioned. On the other hand, dicyanodiamide was found to cause injury to mustard and buckwheat plants, causing the edges of the leaves to become white, and in large amounts to destroy them altogether. Injury to germination by the basic salt and cyanamide would probably not as a rule occur under practical conditions.

The results of manurial experiments, in cylinders, in which oats were manured with sodium nitrate, ammonium sulphate, and calcium nitrate showed that the relative gain in total produce (grain and straw) was as 100:91.9:115.9. Experiments with calcium cyanamide gave conflicting results.

N. H. J. M.

Experiments with Basic Slag-ammonia. BACHMANN (*Biol. Zentr.*, 1908, 37, 423—424; from Fülling's *Landw. Zeit.*, 1908, 55, 808).—The manure contains: P_2O_5 (citrate soluble), 7.15; N as ammonia, 6.77, and CaO, 25.22%. When stored for three months there was a loss of 1.54% of nitrogen as ammonia. Experiments with rye, oats, and grass showed that lower results were obtained with the manure than with a mixture of equivalent amounts of basic slag and ammonium sulphate.

N. H. J. M.

Depression of Growth by Large Amounts of Calcium. C. KANOMATA (*Bull. Coll. Agr. Tōkyō*, 1908, 7, 597—607).—In sand-culture experiments, the yield of oats was reduced 39% by altering the ratio CaO/MgO from 1/1 to 100/1, whilst in soil there was a decrease of 48% when the ratio was altered from 1/1 to 10/1.

Similar results were obtained with rice, barley, buckwheat, mustard, and onion.

An experiment with buckwheat in which powdered magnesite was added in such quantity to the soil injured containing an excess of calcium carbonate that the ratio CaO/MgO was changed from 100/1 to 100,100, slowed a restoration of favourable conditions. It is therefore not the absolute amount of calcium carbonate which is injurious, but its relation to the amount of magnesium present.

N. H. J. M.

Gypsum as a Manure. T. TAKEUCHI (*Bull. Coll. Agr. Tōkyō*, 1908, 7, 583—597).—A large number of pot experiments are described in which peas, barley, oats, beans, rice, and spinach were manured with different forms of phosphoric acid and nitrogen without and with addition of gypsum. Experiments were also made on the effect of gypsum in presence of magnesium alba.

It is shown that calcium sulphate is very beneficial when sodium nitrate is employed, or more generally when any alkaline reaction is produced in the soil. In presence of superphosphate or ammonium sulphate, it tends to depress the yield.

Calcium sulphate is also beneficial in the case of soils containing an excess of magnesium, and may be employed with advantage in the case of spinach, for which calcium carbonate is unsuitable.

N. H. J. M.

Absorption of Varying Amounts of Lime and Magnesia by Plants. T. TAKEUCHI (*Bull. Coll. Agr. Tōkyō*, 1908, 7, 579—581).—Oats were grown in (1) soil in which by addition of calcium carbonate the ratio CaO:MgO was 10:1, and in (2) a control pot

containing soil having a ratio of about 1:1. The following results were obtained:

	Leaves.				Roots.			
	Fresh weight,*	Crude ash,	Per cent. in ash.		Dry weight,	Crude ash,	Per cent. in ash.	
	grams.	per cent.	CaO.	MgO.	grams.	per cent.	CaO.	MgO
1.	106.3	11.97	18.82	4.85	4.4	8.17	32.31	5.69
2.	301.0	12.43	10.94	4.42	13.5	9.45	13.22	6.66

* Including the stems.

The greatest height of the plants of the two pots was (1) 92 and (2) 108 cm., and the number of shoots (1) 32 and (2) 42. N. H. J. M.

Agronomical Equivalent of Artificial Magnesium Carbonate. S. KANAMORI (*Bull. Coll. Agr. Tōkyō*, 1908, 7, 609—612).—The availability of artificial magnesium carbonate is greater than that of the natural substance, owing to difference in composition and to its more finely-divided condition. The results of pot experiments with oats showed that 0.1—0.6 gram of magnesia alba is agronomically equivalent to 5 grams of magnesite, and that larger amounts (in 2.5 kilos. of sand) reduced the yield. Similar results were obtained with barley.

N. H. J. M.

Top-dressing with Magnesium Sulphate. J. N. ZIRKER (*Bull. Coll. Agr. Tōkyō*, 1908, 7, 613—614).—Application of magnesium sulphate, at the rate of 10 kilos. per hectare, to half of a plot which had received slaked lime at the rate of 10,000 kilos. per hectare increased the yield of barley 31%.

N. H. J. M.

Analytical Chemistry.

Apparatus for Testing Burettes and Pipettes; also Mercury Measuring Tubes. O. VON SPINDLER (*Chem. Zentr.*, 1908, i, 1419—1420; from *Schweiz. Woch. Chem. Pharm.*, 1908, 46, 145—148).

—A modification of the Ostwald pipette. The burette to be tested is placed on the long arm of a U-shaped tube, whilst on the shorter arm is placed a standard graduated pipette. Both arms are fitted with glass stopcocks; a third stopcock at the bottom serves for the purpose of emptying the apparatus, and a fourth one regulates the supply of liquid contained in a reservoir, from which the apparatus is filled. By proper regulation of the stopcock, the burette to be tested is filled with water up to the top mark, whilst the calibrated pipette (moist inside) stands at zero. Any quantity of liquid running from the burette through the U-tube can be read off in the standard pipette. In the case of a mercury measuring tube, it may be arranged so that a given volume of mercury forces the same volume of water into the burette.

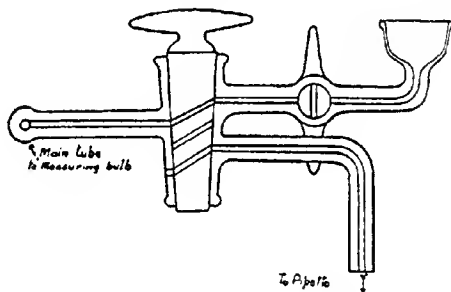
L. DE K.

Circulation Burette. GUSTAV MULLER (*Chem. Zeit.*, 1908, 44, 532).—An ordinary burette is surmounted by a closed stoppered reservoir which is fused on to a large double bored glass tap in such a manner that a liquid may pass through the smaller bore of the tap to the burette, while at the same time the displaced air passes through the second bore of the tap to the top of the closed reservoir. In this manner, the burette may be re-filled without opening to the atmosphere. To allow the burette to deliver the contained liquid, an additional small hole, communicating with the outside, is bored in the large tap.

J. V. E.

New Gas Analysis Apparatus. RAYMOND ROSS and JOHN P. LEATHER (*J. Soc. Chem. Ind.*, 1908, 27, 491).—The apparatus consists of a measuring bulb surrounded by a water jacket; it is provided with a three-way tap and connected by flexible tubing with a mercury reservoir and also with an 800 mm. graduated tube. The measuring bulb communicates with eight absorption pipettes by means of a capillary provided with specially designed taps. The construction of these is shown in the diagram.

By raising the mercury reservoir, the measuring bulb and the whole



of the connexions are filled with mercury, which is allowed to flow through each tap in turn until the small glass cups are about half filled. The reservoir is then lowered so that the mercury falls to the mark on the measuring bulb. The barometric pressure is now read off in millimetres, including the pressure of aqueous vapour, sufficient water for this purpose being introduced with the mercury. The barometer tube is slant off and the measuring bulb re-filled with mercury, the gas to be analysed being introduced and brought exactly to the mark at atmospheric pressure. To introduce the gas into the required absorption pipette, the mercury reservoir is raised, and the mercury in the capillary connecting tubes driven forward into the cups until the gas just reaches the three-way tap. The small tap is then closed, and the absorbent is driven up until it fills the bore of the tap. The tap is next turned so as to allow the gas to enter the pipette. When the absorption is complete, the process is reversed, the gas being swept through the capillary tube into the measuring bulb by means of the mercury in the cup. The mercury is again brought to the mark in

the measuring bulb, connexion with the millimetre tube having been re-established. The reading, multiplied by 100 and divided by the first ("barometric") reading, gives the percentage absorption.

W. P. S.

Metanil Yellow; its use as a Selective Indicator. ERNEST LINDER (*J. Soc. Chem. Ind.*, 1908, 27, 485—488).—Strips of filter paper which have been dipped in a 0.1 solution of metanil yellow (the sodium salt of diphenylamineazo *m*-benzenesulphonic acid) and then dried, are coloured violet when exposed to gases containing vapours of mineral acids, whilst they are unaffected by sulphur dioxide, chlorine, hydrogen sulphide, or acetic acid. The colour change takes place within two minutes in an atmosphere containing 0.016 grain of HCl per cubic foot; with a longer exposure, the limit would probably be extended, as the effect appears to be cumulative. Moisture inhibits the formation of the violet colour, but solutions may be tested for the presence of mineral acid by placing a drop of the solution on a strip of the paper and re-drying the latter at a temperature of 40°. Free mineral acid in vinegar may be detected in this way.

W. P. S.

Estimation of Water of Hydration in Cellulose Materials. CARL G. SCHWALBE (*Zeitsch. angew. Chem.*, 1908, 21, 1321—1323).—Distillation with toluene or petroleum and measuring the layer of water in the distillate gives unsatisfactory results. The water of hydration may, however, be determined indirectly by hydrolysing the cellulose material and estimating the dextrose formed, for only hydrated cellulose is inverted comparatively rapidly. Three grams of the material are boiled with 250 c.c. of 5% sulphuric acid for fifteen minutes in a reflux apparatus, the requisite amount of alkali is added, and the solution is titrated with Fehling's solution.

L. DE K.

Volumetric Process for the Estimation of Chlorates. EDMUND KNECHT (*J. Soc. Chem. Ind.*, 1908, 27, 434—437).—In the method described, titanous chloride solution is employed as a reducing agent. The reaction proceeds according to the equation $6\text{TiCl}_3 + \text{KClO}_3 + 6\text{HCl} = 6\text{TiCl}_4 + \text{KCl} + 3\text{H}_2\text{O}$, and the estimation is carried out as follows: 50 c.c. of standardised titanous chloride solution are run into 5 c.c. of concentrated hydrochloric acid contained in a conical flask through which a current of carbon dioxide is passed. Ten c.c. of the chlorate solution under examination are then added, and, after the lapse of three minutes, potassium cyanate is added, and the excess of titanous chloride is titrated with standardised iron alum solution. All the values being based on an iron standard, the calculation is simple, for six atoms of iron are equivalent to one molecule of chlorate.

W. P. S.

Detection of Potassium Perchlorate in Potassium Chlorate. EDUARD A. KLOBBIE and H. L. VISSER (*Pharm. Weekblad*, 1908, 45, 718—720).—The presence of potassium perchlorate in potassium chlorate can be detected by slowly evaporating an aqueous solution of the mixture with a trace of potassium permanganate on a microscopic slide, the appearance of the mixed crystals being very characteristic.

A. J. W.

Apparatus for the Estimation of Sulphur in Iron and Steel. EDG. RAYMOND (*Bull. Soc. chim. Belg.*, 1908, 22, 181—183).—A combination of von Reis's generating flask (round-bottomed flask with side tube, and fitted with separating funnel) and Heinz-Nowicki's absorbing apparatus (cylinder and worm tube).

The absorption tube has now been fitted with a tube carrying a bulb, which also serves the purpose of a funnel through which the solution of bromine in hydrochloric acid is introduced. There is also a small horizontal outlet tube, which is afterwards connected to a long tube destined to carry off the obnoxious bromine fumes.

The gases given off on dissolving the sample in dilute hydrochloric acid are first passed through an empty bulb and then through the absorber. The last traces of hydrogen sulphide are removed by a current of carbon dioxide. The sulphuric acid formed is then estimated as usual.

L. DE K.

Sodium Peroxide in Certain Quantitative Processes. SAMUEL W. PARR (*J. Amer. Chem. Soc.*, 1908, 30, 764—770).—*Sulphur (and Arsenic) in Pyritic Ores of Iron and Copper.*—A mixture is made of 10 grams of sodium peroxide, 0.5 gram of potassium chlorate, and 0.5 gram of benzoic acid (by careful shaking). 0.25 Gram of the ore is then carefully mixed with the reagent in an improved Parr bomb, where it is ignited by means of a red-hot nickel wire. The fused mass contains the sulphur as sulphate. *Sulphur in Coal, Coke, Ashes.*—The same process is applied, but in the case of coal and coke, 0.5 gram should be taken for analysis, and the benzoic acid be omitted from the mixture. *Sulphur in Indiarubber.*—0.1 Gram of the sample is burnt with the mixture containing 0.3 gram of benzoic acid. *Halogens, Sulphur, &c., in Organic Compounds.*—Instead of the above mixture the following one is used: 10 grams of sodium peroxide and 1.2 grams of "boro-magnesium" mixture (five parts of boric acid, four parts of potassium nitrate, one part of magnesium, all in fine powder), and 0.3—0.5 gram of the organic compound is taken for analysis. The fused mass contains the halogen and the sulphur. The same mixture also serves for the estimation of carbon in *carborundum*. The fused mass contains the carbon as carbonate.

L. DE K.

The Estimation of the Total Sulphur in Urine. ARTHUR KONSCHIEGG (*Plüger's Archiv*, 1908, 123, 274—278).—When the organic matter in urine is oxidised with nitric acid alone, and the sulphur is precipitated as sulphate by barium chloride, the results obtained are too low. This is probably due to loss of sulphuric acid by volatilisation. Better results are obtained if potassium nitrate is added to the mixture of urine and fuming nitric acid.

S. B. S.

Use of Phenolphthalein as Indicator in the Titration of Acids in the presence of Sulphurous Acid. M. ERMASCHI Pozzi-Estori (*Bull. Assoc. Chim. Sucr. Dist.*, 1908, 25, 941—944).—It is shown that, employing phenolphthalein as indicator, the titre of a sulphuric acid solution remains the same after the addition of normal

sodium sulphite as it was before the addition, and consequently this indicator may be used in the presence of sulphurous acid in spite of statements by other observers to the contrary. W. P. S.

Estimation of Nitrogen by Dumas' Method. H. LEEMANN (*Chem. Zeit.*, 1908, 32, 496).—The carbon dioxide used to expel the air from the combustion tube is generated in a separate tube by heating sodium hydrogen carbonate. Between this and the combustion tube is interposed a tube fitted in the middle with a three-way cock. When the supply of carbon dioxide must be temporarily stopped, the stopcock is turned through 90°, and the carbon dioxide still being evolved escapes through a mercury valve.

When the combustion is over, the sodium hydrogen carbonate is heated again, and the stopcock turned into its original position. L. DE K.

Estimation of Phosphorus in Phosphorised Oils. EMIL WÖRNER (*Pharm. Zeit.*, 1908, 53, 398).—Five grams of the oil are treated in a 500 c.c. Jena flask, drop by drop, with 5 c.c. of fuming nitric acid, and, when the first violent action is over, a gentle heat is applied. Ten c.c. of a mixture of equal volumes of sulphuric acid and nitric acid are then slowly added, and the heating continued until the charring action of the sulphuric acid becomes visible. Nitric acid is now added until the violent evolution of brown fumes diminishes. If charring occurs again on heating, more nitric acid should be added. Finally, the whole is heated until sulphuric fumes appear, a few more drops of nitric acid being added if necessary.

The residue, when cold, is boiled with 20 c.c. of water, and the phosphoric acid formed estimated by Neumann's process (precipitating with ammonium molybdate and ammonium nitrate, dissolving the yellow precipitate in excess of $N/2$ sodium hydroxide, boiling off the ammonia, and titrating the excess of alkali with $N/2$ acid, with phenolphthalein as indicator; 1 c.c. of alkali = 0.5536 mg. of phosphorus).

L. DE K.

Estimation of Phosphorus in Phosphor-tin. WILLIAM GEMMELL and SYDNEY L. ARCHBUTT (*J. Soc. Chem. Ind.*, 1908, 27, 427—428).—The following process, in which the phosphorus is evolved as hydride and the latter absorbed and converted into phosphoric acid, is stated to give trustworthy results in the estimation of phosphorus in phosphor-tin. From 2 to 5 grams of the sample are placed in a 500 c.c. flask provided with a two-way tapped funnel and a delivery tube. The gas is absorbed in a set of three Drechsel bottles, the first two containing a depth of about 0.25 inch of bromine, covered by bromine water, and the third, bromine water only. The air is first removed by passing a current of carbon dioxide through the apparatus for five minutes. Concentrated hydrochloric acid is then introduced, the contents of the flask are heated gently until the action has practically ceased, and finally boiled. Carbon dioxide is next passed through the apparatus for a further five minutes to drive any remaining traces of evolved gases into the Drechsel bottles. The contents of the latter are then transferred to a beaker, boiled to

remove the bromine, and the phosphoric acid is precipitated as ammonium magnesium phosphate. If arsenic be present in the sample, it is estimated with the phosphorus and separated subsequently.

W. P. S.

Qualitative Analysis of Phosphates and Other Salts Soluble in Acids. H. CARON and D. RAQUET (*Bull. Soc. chim.*, 1908, [iv], 3, 622—626).—A critical résumé is given of some of the methods at present in use for the analysis of the group III precipitate when this contains phosphates or other salts soluble in dilute acids, and a new method depending on the use of sodium dioxide is described.

The precipitate is suspended in 10% sodium carbonate solution, a little sodium dioxide added, and the solution boiled for a few seconds. After this treatment, the solution will contain any aluminium, chromium, zinc, or uranium that may be present in combination with sodium, as also the acids (oxalic, phosphoric, boric, &c.), whilst in the precipitate will be found manganese (as the hydrated dioxide), iron (as phosphate), and any alkaline-earth compounds, the latter being soluble in acetic acid, by means of which they can be separated from the manganese and iron. Nickel and cobalt should not occur in the group III precipitate in presence of excess of ammonia, but if they do, the cobalt will, after this treatment, occur as the brown oxide and be insoluble in acetic acid, whereas the nickel will be in a form soluble in this acid. A table showing the scheme of separation is given in the original.

T. A. H.

The Reactions of Urine. L. DE JAEGER (*Zeitsch. physiol. Chem.*, 1908, 55, 481—504).—To determine the acidity of the urine, the latter was titrated with sodium hydroxide solution (1) in presence of phenolphthalein alone, and (2) in the presence of phenolphthalein after addition of calcium chloride. The phosphoric acid was also estimated. The phosphates are present in the form of diacid salts. If A represents the acidity, x the phosphates present as Na_2HPO_4 or K_2HPO_4 , y , phosphates present as calcium phosphate, and z those present as magnesium phosphate, and a represents the acidity due to other substances, then Ac_1 (acidity due to direct titration) $= a + x + 1\frac{1}{2}y + 1\frac{1}{2}z$. The acidity determined after addition of calcium chloride, $Ac_2 = a + 2x + 2y + 2z$. Now $2x + 2y + 2z = \text{mgP}_2\text{O}_5/71$ and $Ac = Ac_2 - \text{P}_2\text{O}_5/71$. By three sets of determinations, therefore, the acidity due to the diacid phosphates and the other acidity can be determined. For the theory of the method by means of which the results are arrived at, reference must be made to the original paper.

S. B. S.

Estimation of Carbon in Steel, Ferro-alloys, and Plumbago by means of an Electric Furnace. CHARLES M. JOHNSON (*J. Amer. Chem. Soc.*, 1908, 30, 773—779).—The sample contained in a clay boat is heated inside a steel combustion tube in a current of oxygen, the source of heat being a quartz tube wound with Hoskins' resistance wires. Some alloys, such as ferro-chrome, ferro-boron, &c., require an addition of red lead to facilitate the oxidation. For details, the illus-

tration in the original paper should, be consulted (also compare Abstr., 1906, ii, 630, as to weighing apparatus and purifying train).

L. DE K.

A New Catalyst in Organic Combustion according to the Carrasco-Plancher Method. ORESTE CARRASCO and E. BELLONI (*J. Pharm. Chim.*, 1908, [vi], 27, 469—473. Compare Abstr., 1906, ii, 200, 201).—Instead of mixing the substance to be burnt in a current of oxygen with copper oxide or lead chromate, use is made of platinised, powdered, unglazed porcelain ("biscuit platiné"). This is prepared as follows:

Unglazed porcelain is broken up into powder and passed through a sieve having eighty meshes per cm., and then through another having 400 meshes per cm. The mass remaining on the latter is washed, heated with *aqua regia*, again washed, and then calcined. Fifty grams of the "biscuit" are heated on the water-bath with a solution of 1 gram of platinum tetrachloride in 20 c.c. of water, and, when perfectly dry, an excess of solution of ammonium chloride is added. After six hours, the clear liquid is decanted, and the mass dried and ignited in a platinum crucible. The platinising process is then once more repeated. It is advantageous also to platinise the interior tube of the combustion apparatus which also is constructed of unglazed porcelain.

L. DE K.

Detection of Small Quantities of Carbon Monoxide in Air. JULES OGIER and ÉMILE KOHN-ABREST (*Ann. Chim. anal.*, 1908, 13, 169—173).—The air is introduced into a graduated tube connected at its lower end with a mercury reservoir. The upper part of the tube is surrounded by a water-jacket, and contains a platinum spiral which can be heated by means of an electric current. After the air has been introduced and its volume measured, the platinum spiral is brought to a red heat, then allowed to cool, again heated, and so on until no further contraction in the volume of the air takes place. The pressure and temperature are adjusted before taking the final reading, and the contraction observed corresponds with half the volume of carbon monoxide present. The ignited air is then treated with potassium hydroxide in order to absorb the carbon dioxide formed; the contraction observed is equal to the volume of the carbon monoxide. This second manipulation is necessary in case hydrogen is present in the air under examination. Should the air contain hydrocarbon gases, these must be removed previously in the usual way.

Carbon monoxide and dioxide may be estimated in one portion of air by passing a large measured volume of the latter through a series of vessels containing concentrated sulphuric acid, and pumice and sulphuric acid, then through weighed potash bulbs, and finally through a tube containing iodic acid and surrounded by a steam jacket. The carbon dioxide is absorbed in the potash bulbs, whilst the iodine liberated by the action of the carbon monoxide on the iodic acid is collected in potassium iodide solution and titrated. A current of pure air is employed to drive the sample of air through the apparatus.

W. P. S.

Detection of Small Quantities of Carbon Monoxide in Air. JULES OGIER and E. KOHN-ABREST (*Ann. Chim. anal.*, 1908, 13, 218—224).—The detection is based on the well-known action of carbon monoxide on diluted defibrinated blood and subsequent spectroscopic examination after treating with ammonium sulphide. The volume of air passed before a reaction is obtained gives an idea as to the quantity of carbon monoxide present.

The improvement made by the authors consists in the fact that the air is first deprived of oxygen by means of a solution of sodium hyposulphite.

L. DE K.

Universal Volumetric Method for the Estimation of Magnesium. FERNAND REPITON (*Chem. Zentr.*, 1908, i, 1329; from *Mon. Sci.*, 1908, [iv], 22, i, 33—35).—The solution is evaporated with excess of nitric acid, the residue is taken up with nitric acid, and should phosphoric acid be present, excess of ammonium molybdate is added and the precipitate washed with ammonium nitrate. The filtrate is treated with nitric acid, neutralised with ammonia, and evaporated to dryness. The residue is dissolved in dilute nitric acid and introduced into a measuring flask. A known volume of standardised triammonium phosphate, 2% of citric acid, and ammonia are added, and, after twenty-four hours, the flask is filled up to the mark with ammonia and well shaken. An aliquot part of the filtrate is then titrated with uranium solution for phosphoric acid. The difference in phosphoric acid added and found represents the magnesia.

In the absence of phosphoric acid, the treatment with molybdate is, of course, superfluous.

L. DE K.

Separation of Magnesium from the Alkalis by Alcoholic Ammonium Carbonate. FRANK A. GOOCH and ERNEST A. EDDY (*Amer. J. Sci.*, 1908, [iv], 25, 444—448*).—A modification of Schaffgotsch's process (*Annalen*, 1857, 104, 482). The solution containing about 0.25 gram of the mixed salts is diluted to 50 c.c. and 50 c.c. of absolute alcohol are added. The magnesium is now precipitated by adding 50 c.c. of saturated normal ammonium carbonate solution containing 50% of alcohol, and the whole is left for twenty minutes, stirring every five minutes. The precipitate is collected, washed with the ammonium carbonate solution, dried, ignited, and weighed as magnesium oxide.

If the amount of alkali salts is very large, it is advisable to redissolve the precipitate, after decanting the clear liquid, in the smallest possible amount of hydrochloric acid, and to throw down once more with the precipitant.

L. DE K.

Volumetric Estimation of Zinc. GEORGE C. STONE (*J. Amer. Chem. Soc.*, 1908, 30, 904—905).—A criticism of the paper by Keen on this subject (this vol., ii, 431). The method given for standardising is complicated and untrustworthy. The best way to prepare a zinc solution of known strength is to dissolve some zinc in dilute hydrochloric acid, leaving some of it undissolved, and then dilute with

* and *Zeitsch. anorg. Chem.*, 1908, 58, 427—432.

water so as to have about 5 grams of the metal per litre. The zinc is then estimated in a definite portion of the liquid as pyrophosphate.
L. DE K.

Accuracy of the Colorimetric Estimation of Lead. H. W. WOUDESTRA (*Zeitsch. anorg. Chem.*, 1908, 58, 168—175. Compare Kühn Abstr., 1906, ii, 493).—The colorimetric method for the estimation of small quantities of lead by comparison of the colour of the sulphide in colloidal solution with that of a corresponding solution of known strength, used by several previous investigators, has been tested with fairly satisfactory results, but the presence of iron is a source of inaccuracy. It is important that the amount of electrolyte in the tubes should be the same. To avoid the lengthy evaporation after the first precipitation of the sulphide, Kühn's method of getting the sulphide into a form suitable for filtration by shaking with finely-divided asbestos was found satisfactory, but barium chloride is preferable to sodium nitrate for coagulating the precipitate. After filtration, the sulphide is dissolved in hydrochloric acid, evaporated to dryness, the sulphide reprecipitated, and the process repeated. Finally, the chloride is dissolved in water, 10 c.c. of potassium hydroxide and of a saturated solution of hydrogen sulphide added, and the comparison made.

This method gives more accurate results with small quantities (0.05 mg.) of lead than the volumetric method given by Kühn (*loc. cit.*).
G. S.

Estimation of Lead in Lead-Tin Alloys. SIEGMUND HOLZMANN (*Pharm. Zentr.-h.*, 1908, 49, 417—422).—About 0.5 gram of the alloy is repeatedly oxidised with strong nitric acid in a 200 c.c. platinum crucible with the usual precautions and evaporated to dryness. The residue is treated with 150 c.c. of 10 (vol.) % nitric acid and, without removing the tin oxide, submitted to electrolysis, a platinum dish of about half the size, the outer surface of which has been exposed to a sand blast, serving as electrode. The current should be a weak one, so as to avoid evolution of gas as much as possible. The lead separates as peroxide, and is weighed as such, the last traces of moisture being removed by gently heating the inner side of the dish.
L. DE K.

Detection of Copper and Iron. MARCEL DELEPINE (*Bull. Soc. chim.*, 1908, [iv], 3, 652—654).—The method depends on the production of an intense coloration when a solution of a dialkyldithiocarbamate is added to a solution of a salt of either of these metals in water. The coloured substance produced is extracted with benzene, and the residue left on distilling off the solvent is dissolved in two drops of nitric acid and then ignited. To this residue one drop of nitric acid is added, which dissolves the copper oxide, but leaves the ferric oxide. A few drops of water are added, and the solution decanted into a small vessel, carefully evaporated to dryness, and a drop of a solution of an alkali dialkyldithiocarbamate added, when, if copper is present, an intense yellowish-brown coloration is produced. The residue of ferric oxide is fused with a minute portion of potassium

hydrogen sulphate, and to the fused mass, when cold, two drops of a solution of an alkali dialkyldithiocarbamate are added and then ether; on shaking, the ether develops a pink tint if iron is present. In dealing with solid matter, the latter is incinerated, the ash, dissolved in nitric acid, is re-ignited, and the residue so obtained is treated as described above. The most convenient reagent to employ is a solution of a dialkylamine dialkyldithiocarbamate, which can be made by simply mixing the appropriate dialkylamine with carbon disulphide, and diluting to at least one per cent. strength with alcohol or water. Such a reagent will detect 1 part of copper in 1,000,000 of solution. Colorations are also produced with nickel and cobalt. T. A. H.

Volumetric Estimation of Copper. GEORGE S. JAMIESON, L. H. LEVY, and HENRY L. WELLS (*J. Amer. Chem. Soc.*, 1908, 30, 760—764).—The sulphate solution obtained from the ore in the usual manner is nearly neutralised with ammonia, sulphurous acid is added, and, after heating to boiling, the copper is precipitated with ammonium thiocyanate. The filter containing the washed precipitate is placed in a bottle containing 5 c.c. of chloroform, 20 c.c. of water, and 30 c.c. of hydrochloric acid. The liquid is now titrated, with constant shaking, with standard solution of potassium iodate (11.784 grams per litre; 1 c.c. = 0.002 gram of copper) until the violet colour of the chloroform noticed at first suddenly disappears. L. DE K.

Rapid Method for the Estimation of Mercuric Salts in Aqueous Solution. SAMUEL G. LIVERSIDGE (*Analyst*, 1908, 33, 217—218).—The method depends on the solubility of mercuric iodide in ether, and is particularly applicable to the estimation of small quantities of mercury, as, for instance, in the "liquor hydrargyri perchloridi" of the Pharmacopœia. Twenty-five c.c. of the mercury solution are placed in a separating funnel, and 5% potassium iodide solution is added, drop by drop, until no further precipitate is produced; a large excess must be avoided. A few drops of phosphoric acid solution are next added in order to reduce the solvent action of the excess of potassium iodide on the mercuric iodide, and the mixture is then extracted three times with ether, using about 50 c.c. each time. The ethereal extracts are washed with water, evaporated in a weighed flask, and the residue of mercuric iodide, after being dried at 100°, is weighed. W. P. S.

Acidimetric Estimation of both Mercury Components in Mercury Oxycyanide. ERWIN RUPP (*Pharm. Zeit.*, 1908, 53, 435—436).—0.3 Gram of the sample is dissolved in 50 c.c. of hot water containing 0.5 gram of sodium chloride, and, when cold, titrated with *N*/10 hydrochloric acid, using 1 to 2 drops of 0.2% methyl-orange as indicator. This gives the mercuric oxide only; 1 c.c. of acid = 0.0108 gram of HgO.

1.5 to 2 Grams of potassium iodide and 100 to 125 c.c. of water are now added, by which nontrality is restored, and the titration is repeated. The result represents the mercuric cyanide; 1 c.c. of acid = 0.0126 gram of HgC_2N_2 . L. DE K.

Detection of Manganese and Chromium in the presence of each other. WILLIAM J. KARSLAKE (*J. Amer. Chem. Soc.*, 1908, 30, 905).—To the cold dilute nitric or sulphuric acid solution of the mixture are added 1 to 2 c.c. of silver nitrate reagent and then 2 to 5 grams of potassium persulphate, and the whole is heated until practically no more oxygen is evolved. The manganese and chromium are thus converted into their respective acids, the permanganate colour showing itself first. In order to detect the chromium, the colour of which is obscured by the permanganate, the liquid is cooled and shaken with ether or acetic ether and excess of hydrogen peroxide; the permanganate is decomposed, and the perchromic acid formed dissolves in the ether with a blue colour.

L. DE K.

Oxidising Power of Sodium Peroxide; its use in Qualitative Analysis. DANIEL F. CALHANE (*J. Amer. Chem. Soc.*, 1908, 30, 770—773).—Sodium peroxide in alkaline medium is recommended for the detection of chromium in presence of iron and aluminium. The oxidation, however, goes as far as the perchromate stage, and therefore the usual confirmatory test with lead acetate is not obtained until the liquid has been heated so as to reduce the perchromic acid.

L. DE K.

Simultaneous Qualitative Test for Nickel and Cobalt. HERMANN GROSSMANN and WALTER HEILBORN (*Ber.*, 1908, 41, 1878—1880. Compare Grossmann and Schück, *Ab-tr.*, 1906, ii, 903; 1907, ii, 582).—The presence of both nickel and cobalt may be detected with certainty by the following test: the solution to be examined is concentrated, freed from a large excess of acid, treated with an excess of ammonia, and then with 10—20 c.c. of a 10% sucrose solution; a sufficient quantity of a solution of dicyanodiamidine sulphate is added, and finally sodium hydroxide. The nickel present separates as a yellow, crystalline precipitate of nickel dicyanodiamidine, leaving, in the presence of cobalt, an intense red or reddish-violet solution.

W. H. G.

Estimation of Nickel. M. EMMANUEL POZZI-ESCOT (*Ann. Chim. anal.*, 1908, 13, 186*).—A reply to the criticism of Grossman and Schück (this vol., fi, 230). The author points out that he has laid stress on the fact that the separation from cobalt is accompanied by the formation of the double molybdate, and that he has already indicated the means to be taken to prevent the precipitation of blue cobalt molybdate. He has never claimed that the molybdate process is capable of estimating mere traces of nickel in the presence of cobalt.

W. P. S.

Rapid Estimation of Nickel in the presence of all Elements of Groups 4, 5, and 6. M. EMMANUEL POZZI-ESCOT (*Ann. Chim. anal.*, 1908, 13, 215—216).—The solution is concentrated to a small bulk, and, after neutralising the excess of acid, a large excess of a solution of ammonium molybdate is added, also a little ammonium chloride. The whole is heated to 60—70° and well shaken for a few

* and *Bull. Soc. chim.*, 1908, [iv], 3, 775.

minutes, when it is suddenly cooled. The precipitate, which contains all the nickel, is washed with saturated ammonium chloride solution, and then boiled with water and excess of ammonia for a few minutes. All the nickel is dissolved, and thus separated from any iron, chromium, manganese, and aluminium. If it is feared that the precipitate still retains nickel, it may be redissolved in hydrochloric acid and again treated with ammonia in excess.

The united ammoniacal filtrates are boiled with potassium hydroxide to expel the ammonia, and a little bromine is added to peroxidise the nickel, which is then washed, redissolved in hydrochloric acid, and finally deposited by electrolysis.

L. DE K.

Stannometric Estimation of Alkali Vanadates. T. WARIYANSI and B. MURVANI (*Bull. Soc. chim.*, 1908, [iv], 3, 626—628; *Ann. Chim. anal.*, 1908, 13, 209).—The method depends on the reduction of vanadic acid by stannous chloride in presence of acids. The best results are obtained with a solution containing approximately 2% of stannous chloride and standardised against a solution of iodine of known strength. As indicator, ammonium molybdate, which gives a blue coloration with mere traces of stannous chloride, is used, drops of the indicator being placed on white porcelain. The results are equally good in presence of hydrochloric or sulphuric acid and in either hot or cold solution.

T. A. H.

Electrolytic Estimation of Antimony. O. SCHÖEN (*Zeitsch. Elektrochem.*, 1908, 14, 257—263).—The electrolytic deposition of antimony from a solution containing sodium sulphide and potassium cyanide has been said to yield too high results. Sodium sulphide (80 c.c.; D 1.14) and potassium cyanide (30 c.c.; 30%) are mixed with the neutralised antimony solution, the mixture diluted to 140—150 c.c., and electrolysed in a platinum basin with 1.2 to 1.3 amperes at 60—70°. The voltage must not exceed 1.7 volts. The results obtained are too high with a thickly platinised basin, with wire gauze cathodes, and with rotating electrodes; on the other hand, perfectly correct results are obtained with a polished basin (using not more than 0.1 gram of antimony) and with a very slightly etched or platinised basin, using up to 0.2 gram of antimony. A large excess of sodium hydroxide or too high current density also leads to incorrect results. On a rough surface, the deposit is formed most quickly on the highest points, and so the depressions are bridged over and enclosures of solution are formed which cannot be removed by washing.

T. E.

Electrolytic Estimation of Antimony. ERNST COHEN (*Zeitsch. Elektrochem.*, 1908, 14, 301).—The error in the electrolytic estimation of antimony has been shown by Dormaar (Abstr., 1907, ii, 200) and by Foerster and Wolf (*ibid.*, ii, 508) to be due to oxidation of the antimony, and only to a very small extent to enclosures of mother liquor, as Schöen supposes (preceding abstract).

T. E.

Volumetric Estimation of Antimony. A. KOLB and R. FORMHALS (*Zeitsch. anorg. Chem.*, 1908, 58, 202—208).—In the light of the

results described by the authors (this vol., ii, 599), it is pointed out that antimony, in the form of antimonious acid, can be titrated accurately by the iodine-thiosulphate method when the hydrochloric acid and potassium iodide are used in sufficient concentration; 20—25 c.c. of acid, D 1.125, and 0.5—1.0 grams of the iodide give good results when the total volume is 100 c.c. It is further of advantage to use air-free reagents.

When metallic antimony is dissolved in aqua regia and the excess of nitric acid removed by evaporation, this volumetric method gives results which are about 1% too low, owing probably to incomplete oxidation of the antimony. Accurate results are obtained by the following somewhat complicated method. The metal or a compound is dissolved in aqua regia or in bromine and hydrochloric acid, the nitric acid or bromine removed by evaporation, the solution diluted, the antimony precipitated as sulphide, the latter dissolved in dilute potassium hydroxide, and the mixture oxidised by hydrogen peroxide, first in dilute and then in strong alkali; the solution is then made strongly acid with hydrochloric acid, potassium iodide added, and the titration completed in the usual way.

G. S.

The "Hydrogen Number" as a means for determining Unsaturated Organic Compounds in a manner similar to the Iodine Numbers of Hübl and Wys. SERGIUS FOKIN (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 700—709).—The author defines the "hydrogen number" of an organic compound as the number of c.c. of hydrogen at 0° and 760 mm. pressure absorbed by one gram of the compound. For carrying out the test, the author has devised an apparatus consisting of a distillation flask (50—150 c.c.) having a small beaker fused inside on the bottom and connected by means of the side-tube to a gas burette and a gasometer containing hydrogen. In the small beaker are placed 0.1—0.02 gram of molecular platinum moistened with 0.25—0.5 c.c. of water, and in the flask, the substance to be examined and 20—30 c.c. of alcohol free from dissolved oxygen. The flask is shaken by a shaking machine.

The following are the hydrogen numbers obtained by the author, the values in brackets being either the hydrogen numbers corresponding with Wys' iodine number, or, where indicated, the theoretical hydrogen numbers. Elaidic acid, 78.6—81.4 (78.8); oleic acid, 86.6—87.2 (86.2); fatty acids from sunflower oil, 119.6—120.8 (122.9); fatty acids from linseed oil, 164.9—166.3 (166.0); castor oil, 73.7 (75.5); stearon oil, 260.9 (theoretical 258.4); undecic acid, 115.6 (114.1); stearic acid, 39.4 (65.6); maleic acid, 190.6—191.6 (theoretical 191); acetic acid, 131.0 (theoretical 127.7); citraconic acid, 175.2 (theoretical 171.1); cinnamic acid, 215.0 (150.1). Chlorophyll, naphthalene, benzoic acid, resorcinol, quinol, catechol, pyrogallol, and xylene give zero hydrogen numbers.

T. H. P.

Indirect Estimation of Alcohol by Refraction. ADOLF FRANK (*Chem. Zeit.*, 1908, 32, 569—570).—The indirect estimation of alcohol in worts, beers, wines, cordials, &c., by observing the refraction before and after expelling the alcohol has been shown by the author to be quite untrustworthy.

L. DE K.

Detection of Methoxyl- and Methylimino-groups. JOSEF HERZIG (*Monatsh.*, 1908, 29, 295—297; compare Kirpal, this vol., ii, 436).—Goldschmidt (*Abstr.*, 1905, i, 900) and Herzig and Polak (this vol., i, 546) have shown that tetramethylellagic acid and similar compounds must be heated several hours with hydriodic acid before all the methoxyl groups are completely hydrolysed. In estimating methoxyl groups by Zeisel's method, it is therefore advisable to heat several times with fresh additions of strong hydriodic acid, and to use fresh solutions of silver nitrate, until the latter ceases to become turbid on dilution. Further, the presence of a methoxyl- and not a methylimino-group is only indicated with certainty when the theoretical quantity of methyl iodide is liberated in the time normally required for the estimation of methoxyl by Zeisel's method (compare Herzig and Meyer, *Abstr.*, 1895, ii, 296; 1898, i, 53).

W. H. G.

Bang's Method of Estimating Sugar. H. JESSEN-HANSEN (*Biöchem. Zeitsch.*, 1908, 10, 249—257. Compare Abstr., 1906, ii, 136).—This method was tested, and is highly commended.

W. D. H.

The Reduction of Cuprous Oxide in the Estimation of Reducing Sugars. VLADIMÍR STANĚK (*Zeitsch. Zuckerind. Böhm.*, 1908, 32, 497—499).—The cuprous oxide obtained by the action of a reducing sugar on Fehling's solution is collected on a layer of asbestos in a Gooch porcelain or copper crucible and washed in the usual way. The crucible is then gently heated over a spirit-flame, and immediately suspended in a beaker containing a small quantity of 70% methyl alcohol, the beaker being heated with a small flame, so that it is filled with vapours of methyl alcohol. The latter reduce the cuprous oxide to metallic copper, and the crucible and its contents are then dried at a temperature of 100° and weighed. Before use, the crucible containing a layer of asbestos is submitted to similar treatment.

W. P. S.

Colour and Spectral Reactions of Sugars with Naphtharesorcinol and Hydrochloric Acid. BERNHARD TOLLENS and F. ROBIWE (*Zeitsch. Ver. deut. Zuckerind.*, 1908, 629, 521—526; *Ber.*, 1908, 41, 1783—1787).—The authors have examined the colour reactions of a number of sugars and allied substances with naphtharesorcinol and hydrochloric acid. A few grains of the sugar and about the same quantity of naphtharesorcinol are mixed in a test-tube with 10 c.c. of a mixture of equal volumes of hydrochloric acid, D 1.19, and water, and the liquid heated slowly to gentle boiling, which is maintained for one to three minutes. After three to five minutes, the tube is cooled, the solution filtered, and the residue on the filter washed three or four times with water until the wash-water becomes colourless. Alcohol, 95° Tr, is then poured on to the filter, and the alcoholic solution of the residue passing through is examined spectroscopically.

When gently warmed with naphtharesorcinol and hydrochloric acid, lævulose and sorbose give a fine red coloration, which is somewhat more violet than that given by lævulose with resorcinol. Dextrose

and mannose, as well as substances which yield these sugars when hydrolysed, give, when treated as above, faintly fluorescent alcoholic solutions, which exhibit a band in the green portion of the spectrum. In absence of levulose, galactose and galactosides yield alcoholic solutions showing a band on the *D*-line and one in the green; if levulose is present, it may be destroyed beforehand by heating with the diluted hydrochloric acid. With pentoses, and more especially with methylpentoses, the green fluorescence of the alcoholic solutions obtained is very marked; the methylpentoses yield violet-blue alcoholic solutions, which exhibit a band on the *D*-line and another in the green. Glycuronic acid gives a fine blue alcoholic solution showing a band on the *D*-line.

T. H. P.

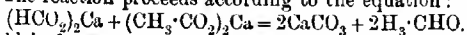
Simple Method of Detecting Glycuronic Acid and its Derivatives in Presence of Pentoses and in Urine. BERNHARD TOLLENS (*Zeitsch. Ver. deut. Zuckerind.*, 1908, 829, 526—528; *Ber.*, 1908, 41, 1788—1790. Compare preceding Abstract).—Glycuronic acid may be readily detected as follows. A piece of the substance to be examined as large as a pea is heated in a wide test-tube with 5—6 c.c. of water, 0.5—1 c.c. of a 1% alcoholic naphtharesorcinol solution, and 6—7 c.c. of hydrochloric acid, D 1.19, the liquid being kept gently boiling for a minute. After standing for four minutes, the liquid is cooled, mixed with an equal volume of ether, and well shaken. When the liquid has settled, the upper ethereal solution has a blue or red colour, exhibits blue fluorescence, and has a band slightly to the right of the *D*-line if glycuronic acid is present; 0.1%, or even less, of glycuronic acid can be detected by this reaction, which is also given by compound glycuronic acids and by various plants, for instance, *Fucus* and *Laminaria*.

T. H. P.

The Quantity of Formic Acid in Honey. K. FARNSTEINER (*Zeitsch. Nahr. Genussm.*, 1908, 15, 598—604).—It is shown that only very small quantities of free formic acid (from 0.0011 to 0.0024%) occur in honey, the greater part of the acidity of the latter being due to some other acid, possibly malic acid. About 0.02% of formic acid is present in a combined state, probably as an ester.

W. P. S.

Detection of Formic Acid in Foods. ALPHEUS G. WOODMAN and A. L. BURWELL (*Tech. Quarterly*, 1908, 21, 1—3).—In the method proposed, the formic acid is converted into its calcium salt, and the latter is subjected to dry distillation in the presence of calcium acetate. The reaction proceeds according to the equation:



The acetaldehyde formed is then detected by means of magenta-sulphurous acid reagent. The details of the method are: 50 grams of the sample are acidified with 20 c.c. of 20% phosphoric acid and steam distilled until about 200 c.c. of distillate have been collected. To the distillate are added 2 c.c. of 30% acetic acid and 20 c.c., or more, of milk of lime, and the solution is evaporated to dryness. The dry residue is then transferred to a test-tube provided with a bent delivery tube, and is there subjected to dry distillation. The distillate is

collected in a little water, and the solution is treated with the magenta-sulphurous acid reagent. A slight coloration nearly always develops, even in the absence of formic acid, and the latter must not be considered to have been present in the sample unless the coloration obtained exceeds that of a solution prepared by diluting 8 c.c. of cupric chloride solution (12 grams of the crystallised salt per litre) and 12.5 c.c. of cobaltous chloride solution (24 grams of the crystallised salt and 100 c.c. of hydrochloric acid per litre) with water to 100 c.c. If the food contained 0.05 per cent. of formic acid, the coloration obtained will be about six times as dark as that of the comparison solution.

W. P. S.

Detection of Citric Acid in Wine, &c. G. FAVEEL (*Ann. Chim. anal.*, 1908, 13, 177—179).—When citric acid is heated with sulphuric acid, formic and acetonedicarboxylic acids are formed; the latter acid may then be separated and identified. In testing wine, 100 c.c. are evaporated to dryness on the water-bath, the residue is dissolved in 7 c.c. of boiling water, and to the solution are added 35 c.c. of 95% alcohol. At the end of thirty minutes, the mixture is passed through a filter, and the filtrate is treated with 0.4 gram of calcium acetate dissolved in 5 c.c. of water. The calcium citrate which is precipitated (if citric acid is present in the wine) is collected on a filter and, when dry, transferred to a test-tube, 3 c.c. of concentrated sulphuric acid, heated previously to 100°, are added, and the solution is kept at a temperature of 80° to 90° for two minutes. It is then cooled, diluted with three times its volume of water, again cooled, and shaken with alcohol-free ether. On evaporating the ethereal solution, acetonedicarboxylic acid crystallises out; when dissolved in water, this acid gives a characteristic violet-red coloration with ferric chloride. The test is not affected by the presence of formic, acetic, butyric, tartaric, malic, lactic, or oxalic acids in the wine or other liquid under examination, but salicylic acid must be removed previously by extraction with ether after acidifying with hydrochloric acid. The method will detect 0.005% of citric acid in wine.

W. P. S.

Citric Acid and Natural Wines. H. ASTRUC (*Ann. Chim. anal.*, 1908, 13, 224—226).—The author states that natural wines may contain citric acid. The presence of this acid is detected with safety by Denigès' reagent (ministerial decision, Jan. 18, 1907).

L. DE K.

The Normal Citric Acid of Wines. GEORGES DENIGÈS (*Ann. Chim. anal.*, 1908, 13, 226—227).—The author states that he has noticed ten years ago that new wines contain 3—6 centigrams of citric acid per litre as a natural constituent.

Probably owing to bacterial influences, the acid cannot be detected in some old samples.

L. DE K.

Phenolsulphonic Acid and its Salts. GERHARD HÜBENE (*Chem. Zeit.*, 1908, 32, 485—486).—The phenol group is but in

perfectly precipitated by bromine, and cannot therefore be titrated by the usual volumetric bromine and iodine methods. On boiling, however, with a saturated solution of bromine in hydrochloric acid, the phenol is completely eliminated, whilst the sulphonyl group is converted into sulphuric acid, which may then be estimated in the filtrate as usual. From this should be deducted any free sulphuric acid the compound may contain, which is estimated by simply adding barium chloride and a few drops of hydrochloric acid. L. DE K.

The Freezing Point of Milk. A Method of Detecting Adulteration. W. R. GELSTON ATKINS (*Chem. News*, 1908, 97, 241—242).—The results of a considerable number of determinations are given, showing that the freezing point of milk is practically a constant, namely, -0.55° ; the variations from this rarely exceed 0.03° above or below the mean. Determinations of the freezing point and specific gravity of a sample of milk are sufficient to show whether water has been added or fat removed. The freezing point of milk is not affected by the presence or absence of fats. W. P. S.

Flask for Fat Estimation. WILBUR L. DUBOIS (*J. Amer. Chem. Soc.*, 1908, 30, 797—798).—The flask recommended by Wheeler and Hartwell (*Abstr.*, 1901, ii, 586) and modified by Robison has been replaced by one of the Erlenmeyer type. The flask is fitted to the condensing apparatus by means of a seal consisting of a maple cup made to fit over an ordinary rubber stopper through which passes the neck of the flask. The seal is made by mercury in a manner similar to the device used by Wheeler and Hartwell. L. DE K.

New Method for the Estimation of Fat in Cocoa. ADOLF KREUTZ (*Zeitsch. Nahr. Genussm.*, 1908, 15, 680—683).—A weighed portion of about 1.5 grams of the cocoa is placed in a small flask, 3 grams of solid chloral alcoholate are added, and the mixture is heated on a water-bath until melted to a homogeneous mass. About 15 c.c. of ether are next added, and the contents of the flask are shaken; a further quantity of 35 c.c. of ether are then added, and the mixture is poured on a filter, the ethereal filtrate being received in a weighed flask. The residue on the filter is washed twice with ether, the washings being also collected in the flask, from which the ether is then evaporated, and the residue of fat dried at a temperature of $105-110^{\circ}$ and weighed. The chloral alcoholate is expelled completely from the fat at this temperature. W. P. S.

The Ethyl Ester Value of Fats. A New Constant for the Detection of Coconut Oil. JOSEF HANUS and LAD. ŠTEKL (*Zeitsch. Nahr. Genussm.*, 1908, 15, 577—587).—The process is based mainly on the different amounts of lauric acid occurring in coconut oil and other fats. The glycerides are converted into ethyl esters and the volatile portion of these is distilled and estimated. Five grams of the filtered fat to be tested for coconut oil are placed in a 200 c.c. Erlenmeyer flask and heated for fifteen minutes to a temperature

of 50°. Thirty c.c. of *N*/10 alcoholic potassium hydroxide solution are then added, the contents of the flask are shaken until a clear solution is obtained, and again heated for ten minutes at 50°. Two c.c. of sulphuric acid (which quantity must be capable of exactly neutralising the 30 c.c. of alkali added) are then added, the whole is diluted with water to a volume of 145 c.c., and distilled, a little pumice-stone being added. The first 30 c.c. of alcoholic distillate are rejected, whilst the next 100 c.c. are collected and transferred to a flask. Alcohol is added until the turbid solution becomes clear, and the free acid is titrated, using phenolphthalein as indicator; 40 c.c. of *N*/2 alcoholic potassium hydroxide solution are added, the solution is boiled for forty-five minutes under a reflux apparatus, and the excess of alkali is then titrated. The quantity of alkali required for the saponification, expressed in c.c. of *N* 10 solution, is termed the ethyl ester value of the fat. This value for various fats is: coconut oil, over 40; palmnut oil, about 25; butter, from 7 to 14; lard, cacao butter, sesame oil, cotton oil, olive oil, &c., less than 3. The value is particularly useful for detecting the presence of coconut oil in lard, cacao butter, and margarine, but it will not indicate, with certainty, a less quantity than 15% of this oil in butter.

W. P. S.

Abraistol. DIOSCORIDE VITALI (*Boll. chim. farm.*, 1908, 47, 291—301).—Abraistol, or calcium β -naphthol- α -sulphonate, is used as an internal antiseptic and as a precipitant for tartrates in wine, instead of other calcium salts. A number of colour reactions are described, one of the best being that obtained by evaporating with a solution of mercurous nitrate (reddish-violet colour). From wine, the acid may be extracted by amyl alcohol or ethyl acetate, or it may be isolated as potassium salt on evaporating the wine, after making it alkaline, and extracting the residue with alcohol; the acid can then be further purified by lead acetate and hydrogen sulphide. G. B.

Gall-Iron Inks. ERICH KEDESZY (*Chem. Zentr.*, 1908, i, 591; from *Mitt. K. Materialphys.-Unt.*, 25, 268—269).—*Detection of Tannin and Gallic Acid with Molybdate Solution.*—Tannin and gallic acid give with acid ammonium molybdate solution a sherry or even dark brown coloration. The residue obtained from the extraction with ethyl acetate (see this vol., ii, 544) is dissolved in 100 c.c. of water, 1—2 c.c. are diluted to 25 c.c., and mixed with 5 c.c. of Finkener's molybdate solution.

An approximate estimation may be made by comparing the depth of colour with a standard solution. This may be made by extracting an ink of known composition with ethyl acetate and proceeding as already directed. L. DE K.

A Colour Reaction of Histidine. FRANZ KNOOP (*Zeitr. chem. Physiol. Path.*, 1908, ii, 355).—On adding bromine water to an aqueous solution of histidine or a histidine salt, decolorisation at first takes place. On further addition of the reagent, the mixture assumes a permanent yellow colour; on warming, it again becomes at first

colourless, but after a time a pink colour appears, which afterwards deepens to a deep wine-red. Later, black, amorphous particles separate from the solution. Too large an excess of bromine destroys the reaction. A number of iminoazole derivatives nearly allied to histidine fail to give the reaction. The reaction is sensitive with solution of 1 in 1000. S. B. S.

Alkaloid Reactions (Tropacocaine). C. REICHARD (*Pharm. Zentr. h.*, 1908, 49, 337—342).—A series of tests is given of which the following are examples. When examined with a magnifying glass, tropacocaine hydrochloride shows a strong double refraction, and exhibits all the colours of the rainbow. When moistened with water, it gives no aromatic odour, thus distinguishing it from cocaine. Warmed with potassium ethyl sulphate and sulphuric acid, it gives the odour of ethyl benzoate, whilst cocaine gives a strong odour of peppermint.

Sulphuric acid gives no characteristic colour. The reactions with sodium nitroprusside and with copper sulphate are very much like those obtained with cocaine. A more characteristic reaction is obtained with nitric acid. On evaporating with nitric acid to dryness, an opaque, white residue is obtained; cocaine yields a transparent, varnish-like substance. The behaviour with cobalt nitrate is also important. If to a small drop of cobalt nitrate is added a slight excess of tropacocaine hydrochloride, the mixture turns yellow; on warming, the colour changes to blue, but on cooling the yellow colour is restored. Cocaine when treated similarly yields a permanent blue spot. L. DE K.

Estimation of Albumin in Urine by Esbach's Method. J. C. VAN DER HARST (*Pharm. Weekblad*, 1908, 45, 489—492).—A criticism of the popular Esbach albumimeter, the indiscriminate use of which has already been condemned by various authorities. It now appears that some urines contain a colloidal substance which prevents the formation of the albumin picrate; this may, however, be eliminated by boiling the urine with strong acetic acid, but in such a case a different apparatus would have to be constructed. L. DE K.

Reaction between Hæmoglobin and the Leuco-base of Malachite-green. GEORGE A. BUCKMASTER (*Proc. physiol. Soc.*, 1908, xi—xiv.; *J. Physiol.*, 37).—This base (tetramethyldiamino-triphenylmethane), first used by Adler for the detection of blood, is recommended for that purpose. Like the guaiacum reaction, the bluish-green colour developed is not due to the chlorides of blood (as Senter suggested) or to any ferment, but to the iron in hæmoglobin and its derivatives. It is termed a pseudo-peroxydase reaction. W. D. H.

Sensitive Reaction for Carboxy. ANGELO DE DOMINICIS (*Boll. chim. farm.*, 1908, 47, 258—260).—The author finds that the tannic acid test for carboxy-hæmoglobin can be controlled by

examining the mixture of blood and tannic acid solution spectroscopically by means of reflected light. He uses Schulz's modification of this test, according to which 2 c.c. of blood, diluted to 10 c.c. with water, are shaken with 10 c.c. of 3% aqueous tannic acid solution; with normal blood, a brick-red colour is formed, which changes to brownish-grey, whilst blood containing carbon monoxide yields a persistent rose-red coloration. The spectroscopic examination is made twenty-four hours after the tannic acid has been added to the blood. The normal blood then exhibits a band in the red, whilst the bands due to the hæmoglobin are scarcely visible; when carbon monoxide is present, either no band or only a light one appears in the red, whilst the hæmoglobin bands are much more intense.

T. H. P.

Composition of Meat Extract. KARL MICKO (*Zeitsch. Nahr. Genussm.*, 1908, 15, 449—462).—The main part of the paper is devoted to the behaviour on hydrolysis of those constituents of meat extract which remain in solution after saturating the liquid with zinc sulphate. They are recovered from the filtrate by evaporating in a vacuum and extracting the dry residue with ammonia and alcohol (1:3).

When, after the purification with lead hydroxide, &c., the syrupy mass is boiled with hydrochloric acid, most of the matter is precipitated by phosphotungstic acid (diamino-acids). From the filtrate may then be recovered: taurine, glyoxime, alanine, leucine, aspartic acid, and glutamic acid; for working details, the original article should be consulted.

L. DE K.

The Mechanism of the Guaiacum Reaction. C. F. CARLSON (*Zeitsch. physiol. Chem.*, 1908, 55, 260—294).—The theory is advanced that the blue coloration of guaiacum tincture takes place in those reactions in which the atoms of water are in a "labile" condition and readily combine, as in the reaction $\text{NaOH} + \text{HCl} = \text{NaCl} + \text{H}_2\text{O}$. It is to the formation of water in such reactions that the blue coloration is due. There are certain exceptions, such as the reaction of sulphuric acid on zinc hydroxide, but a theory is advanced to explain why water is not formed in such reactions, but a stable hydrate. A theory is also advanced to explain the hydrolysis by means of enzymes, and to show why the latter give the guaiacum reaction.

S. B. S.

Criticism of Joulie's Process for Estimating the Acidity of Urine. FERNAND REPTON (*Ann. Chim. anal.*, 1908, 13, 147—148. Compare Abstr., 1907, ii, 409).—A controversy with Joulie on the subject of acidity in urines (compare Joulie, *Clinique et laboratoire*, Aug., 1907).

L. DE K.

General and Physical Chemistry.

The Ultimate Rays of the Metalloids, Tellurium, Phosphorus, Arsenic, Antimony, Carbon, Silicon, and Boron. ANTOINE DE GRAMONT (*Compt. rend.*, 1908, 146, 1260—1263. Compare Abstr., 1907, ii, 517).—Alloys of lead or tin with 10% to 0.001% of the metalloids mentioned in the title have been examined spectroscopically, and the ultimate rays of great persistence found to coincide with those previously observed in minerals containing the same metalloids. The lines are common to the arc and spark spectra, with or without condensation, and are not masked by the presence of other substances. They are all situated in the ultra-violet, and can only be photographed when prisms of quartz or calc spar are employed. W. O. W.

The Red Portion of the Calcium Chloride Arc Spectrum. C. F. O. MEISENDACH (*Zeitsch. wiss. Photographie, Photophysik. Photochem.*, 1908, 6, 258—270).—The red end of the calcium arc spectrum has been studied photographically by means of red-sensitive plates, a large Rowland grating being used. The number of bands observed is very large, and only a few of them can be resolved. Since the bands are sometimes degraded towards the red and sometimes towards the violet, it appears that bands of different origin, due probably to the chloride, the oxide, and the metal, occur together. Detailed measurements of the bands and of the line spectrum are given. Four groups of bands are found to obey Deslandres' law. C. H. D.

The Separation and Quantitative Spectra of Cerium, Lanthanum, and Didymium. JAMES H. POLLOCK and A. G. G. LEONARD (*Sci. Proc. Roy. Dubl. Soc.*, 1908, 11, 257—269).—The separation of cerium from mixed cerite earths by the action of chlorine in alkaline solution is recommended, fusion of the nitrates being employed to separate lanthanum, didymium, and yttrium. Neodymium and praseodymium were not separated. The residual lines on sparking dilute solutions between gold electrodes have been recorded and photographed in the manner already described (Abstr., 1907, ii, 918). C. H. D.

The Quantitative Spectra of Molybdenum, Tungsten, Thorium, and Zirconium. A. G. G. LEONARD (*Sci. Proc. Roy. Dubl. Soc.*, 1908, 11, 270—279. Compare preceding abstract).—The lines observed on sparking solutions containing 1, 0.1, 0.01, and 0.001% of the element between gold electrodes have been measured and photographed. The most persistent lines occur in the more refrangible part of the spectrum. The vibrations of small wave-length are therefore the most easily excited. This explains the greater tendency of ultra-violet rays to induce chemical action. C. H. D.

A New Arrangement of the König Spectrophotometer and its Application to the Determination of Chemical Equilibria. JOEL HILDEBRAND (*Zeitsch. Elektrochem.*, 1908, 14, 349—353).—Two small tungsten filament lamps are connected in series so that variations of current affect them equally. The light from one lamp passes through the solution. The two beams are then polarised at right angles to each other, pass a direct vision prism, and are received by a telescope with a Nicol prism in the eye-piece. The telescope can be adjusted to receive light of any desired wave-length; by rotating the Nicol, the two beams can be made of the same intensity.

The dissociation of phenolphthalein is measured by means of the instrument. Phenolphthalein is dissolved in solutions of ammonia and ammonium chloride in which the concentration of the hydrogen ions is known. The amount of phenolphthalein dissociated is obtained by comparing the absorption with that observed in a completely dissociated solution. The dissociation constant, $[H^+][R^-]/[HR]$, where $[R^-]$ is the concentration of the phenolphthalein ion, is found to be 1.7×10^{-10} for solutions in which from 5 to 65% of the phenolphthalein is dissociated; for smaller degrees of dissociation smaller values are observed.

T. E.

Optical Investigation of the Condition of Chromate and Permanganate Solutions. ARTHUR HANTZSCH and ROBERT H. CLARK (*Zeitsch. physikal. Chem.*, 1908, 63, 367—381).—By a study of absorption spectra and determination of molecular extinction coefficients, the authors have reached results for chromates, dichromates, and permanganates similar to those already reached for platinumchlorides (see this vol., ii, 447).

Solutions of chromium trioxide in pure water and in aqueous sulphuric acid are at all concentrations optically identical with each other and with feebly acid solutions of potassium dichromate. Solutions of the latter in pure water deviate very slightly in the direction of monochromate solutions. Solutions of monochromates in pure water, in alkalis, and in methyl alcohol are at all concentrations quite different from dichromate and chromic acid solutions in their optical characteristics, but are identical among themselves except for a slight deviation of the pure aqueous solutions in the direction of the dichromate solution. The optical characteristics are independent, not only of the concentration and the solvent, but also of the temperature.

The chromophoric group in all acid solutions is the completely saturated complex Cr_2O_7 ; in all alkaline solutions the corresponding complex CrO_4 . From the optical point of view, it is immaterial whether these complexes are combined with hydrogen or alkali metal, dissociated or undissociated; the colour of the ions must be the same as that of the undissociated molecule.

Similarly, the absorption of permanganic acid and its salts is not appreciably influenced by the solvent, the temperature, or the degree of dissociation.

Emphasis is laid on the value of this optical method in studying constitutive changes due to the chemical influence of the solvent.

J. C. P.

Attempt to Produce Dichroism by Pressure in Silver Haloids. FELIX CORNU (*Centr. Min.*, 1908, 393—395).—A. von Lasaulx, in 1879, made the observation that dichroism is developed by pressure in crystals of chlorargyrite from Schneeberg, but the present author has been unable to confirm this observation by his experiments on chlorargyrite, embolite, and bromyrite from various other localities.

L. J. S.

Apparatus for Producing Flame Colorations and Other Changes of a Non-luminous Flame. F. SCRIBA (*Chem. Zentr.*, 1908, i, 1753; from *Zeitsch. physik-chem. Unterr.*, 1908, 21, 110—111).—A modified form of Bunsen burner made of glass and having a glass tube bent downward as air inlet. By this means a flame coloration is obtained by introducing the air inlet tube into a vessel containing the vapour or dust of the flame colouring substances.

J. V. E.

Polarimetric Measurements with Small Quantities of Liquid. JULIUS DONAU (*Monatsh.*, 1908, 29, 333—336).—In the experiments in question, a capillary tube of 0.4—0.5 mm. internal diameter and 5—10 cm. long, made of black glass, was fixed by means of rubber tubing into a wider tube; the liquid to be examined was then introduced, the ends closed with small glass covers, the tube pushed inside an ordinary polarimeter tube, and the measurements made in the usual way. Sodium light or, for the longer tubes, electric light is used, and the results are scarcely less accurate than those obtained in the ordinary method (compare Fischer, this vol., i, 544).

G. S.

Dispersion of Magnetic Rotatory Power in the Neighbourhood of Bands of Absorption in the Case of Rare Earths. JEAN BECQUEREL (*Phil. Mag.*, 1908, [vi], 16, 153—161. Compare Abstr., 1906, ii, 317, 421; 1907, ii, 147; this vol., ii, 78, 338).—In reference to recent communications of Wood (this vol., ii, 244) and Elias (this vol., ii, 549), the author discusses the results of his work on the influence of a magnetic field on the absorption bands of xenotime and tysonite, details of which have already been published.

It is maintained that the experimental observations are in agreement with the theory of magnetic rotatory polarisation, which is based on the Hall effect. The phenomenon in the case of crystalline substances is of the same nature as that found by Zeeman for vapours.

Differences are found in that the order of magnitude of the displacements for many of the bands of crystals is much greater than for the bands of vapours, and that when the optic axis of a uniaxial crystal is parallel to the lines of force of the field and the direction of propagation of the light, the bands corresponding with the absorption of the circular components of given sense are not all displaced in the same direction.

H. M. D.

Photographic Capacity and Supposed Radioactivity of Hydrogen Peroxide. OCTAVE DONY-HENAUULT and ALICE DONY-HENAUULT (*Bull. Soc. chim. Belg.*, 1908, 22, 224—245. Compare Abstr., 1906, ii, 645).—The results of this work show that Russell's

view, that the latent images produced by various organic materials when placed on sensitised plates in the dark are due to the action of vapour of hydrogen peroxide directly evolved by these materials, is accurate, and that the action is not due to radiation, as suggested by Graetz (*Physikal. Zeit.*, 1904, 5, 698).

The vapour tensions of solutions of hydrogen peroxide have been ascertained by determining the amount of the peroxide carried away in a certain time by a known current of gas from a solution of the peroxide of known strength kept at a definite temperature. The peroxide was absorbed in a solution of titanous anhydride in sulphuric acid, and finally estimated by a standard solution of permanganate. At constant temperature, the vapour tension of hydrogen peroxide solution increases with the concentration, but for equal concentrations the partial vapour pressure may diminish with rise of temperature; thus a solution may give more water vapour and less hydrogen peroxide vapour at 40° than at 19° (compare Precht and Otsuki, *Abstr.*, 1905, ii, 296, 495). The vapour tensions observed are tabulated in detail in the original. The minimum quantity of hydrogen peroxide necessary to produce an image on a photographic plate is 1.2×10^{-2} gram. The vapour tension and photographic activity of hydrogen peroxide solution may be either increased or diminished by the addition of sulphuric acid, and, generally, parallel observations are concordant, but influences sometimes disturbing this concordance are (1) the slow inter-action of the acid and peroxide, causing the vapour tension to vary with the duration of the experiment, and (2) the effect of increased humidity in intensifying the image on the plate.

From these observations, the conclusion is drawn that the photographic activity of solution of hydrogen peroxide is due to the actual transport of peroxide vapour to the sensitised layer of the plate. Incidentally, it is pointed out that the photographic method may be applied to the determination of the molecular structure of the unstable compounds of titanous anhydride and other oxides with hydrogen peroxide by noting the concentration of peroxide at which the solutions of the anhydride and peroxide in sulphuric acid begin to affect photographic plates, this being the point at which the anhydride has been saturated with peroxide. Results of such experiments indicate that the compounds $\text{TiO}_2 \cdot \text{H}_2\text{O}_2$ and $\text{MoO}_3 \cdot 2\text{H}_2\text{O}_2$ exist, which are stable in sulphuric acid solution.

F. A. H.

Radioactivity of Ordinary Metals and the Penetrating Radiation from the Earth. J. C. McLENNAN (*Physikal. Zeitsch.*, 1908, 9, 440—443).—The electrical conductivity of the air enclosed in cylinders of lead, aluminium, and zinc has been measured at a number of places in the neighbourhood of Toronto. The collected data lead the author to draw the conclusion that if the metals could be entirely freed from radioactive impurities, and if observations could be made under conditions such that penetrating radiations from external sources could be excluded, the conductivity of the enclosed air would have an extremely small value, and might disappear completely.

H. M. D.

Helium and Radioactivity in Rare and Common Minerals. ROBERT J. STRUTT (*Proc. Roy. Soc.*, 1908, 80, A, 572-594).—A large number of minerals, including sulphides, native elements and oxides, rare earth minerals, and igneous rocks, have been tested for the inert gases, more particularly helium. The general method of procedure was to heat the finely powdered mineral to redness, absorb the ordinary gases given off, and examine the spectrum of the inert residue.

Practically all the minerals contain helium, and in the majority of cases in the proportion to be expected from the traces of uranium and radium which the minerals contain. Thus for samarskite, hematite, and quartz, which contain 1,500,000, 700, and 2 c.mm. of helium per kilogram respectively, the ratio of helium to uranium oxide varies only from 9:1 to 14:1. In a few cases in which the ratio is higher, the mineral contains thorium, apparently in sufficient amount to account for the greater helium content. The only exception to the above statements is beryl, which yields a proportion of helium much greater than corresponds with the amount of radioactive substance present. ●

The only minerals which contain appreciable amounts of argon are igneous rocks, and there does not appear to be any connexion between the radioactivity and the proportion of argon present. The results, therefore, afford no evidence that argon is one of the products of radioactive change.

G. S.

Radioactivity of Mineral Springs in the Tyrol. MAX BAMBERGER (*Monatsh.*, 1908, 29, 317-332).—The measurements were made by Engler's method (*Abstr.*, 1907, ii, 218). The temperature and the radioactivity (in electrostatic units) of the water from a large number of wells are given in tabular form, as well as some geological notes on the localities. The radioactivity of sediments from four of the wells has also been determined.

G. S.

Radium Content of Deep-Sea Sediments. JOHN JOLY (*Phil. Mag.*, 1908, [vi], 16, 190-197).—The author has examined the radioactivity of deep-sea sediments obtained from the "Challenger" and "Albatross" collections, and, further, of a specimen of *Globigerina* Ooze, and one of the mud thrown up by the volcanic disturbance of 1906 in the Bay of Bengal. These sediments are very much richer in radium than average terrestrial rocks. The richest sediments are those from the most central parts of the Pacific Ocean. Comparing the amounts of radium and calcium carbonate in the deposits, it is found that as the former increases, the latter decreases. This indicates that the amount of radium increases with the antiquity of the sediment. The largest amount of radium found was in the red clay from the Challenger Station, 276; per gram of air-dried material it contains 52.6×10^{-12} gram radium. Uranium has been found to be present in this red clay; a colorimetric determination of the amount present in the 8.42 grams examined gave 0.0006 to 0.0007 gram, whereas the amount calculated from the radium content is 0.0012 gram.

H. M. D.

Influence of Temperature on Radioactive Changes. WILHELM ENGLER (*Ann. Physik.*, 1908, [iv], 26, 483—520. Compare Curie and Danne, Abstr., 1904, ii, 306; Bronson, Abstr., 1905, ii, 567; Makower, Abstr., 1906, ii, 259; Makower and Russ, Abstr., 1907, ii, 421; this vol., ii, 449; Schmidt, this vol., ii, 141).—A further attempt to settle the question whether the rate of decay of radioactive substances is independent of the temperature. The measurements were made on radium *B* and *C* and on radium emanation, the experiments being so arranged that the rate of decay could be measured during the period of heating and also immediately afterwards.

The observations with radium *B* and *C* indicate definitely that the rate of decay at 1100° to 1400° is greater than at the ordinary temperature, whilst, after cooling, the rate of decay is for some time less than the normal value. The influence of temperature on the rate of decay increases with the temperature.

In a similar way, when radium emanation is heated to temperatures above 1100°, an increase in the activity amounting to several units per cent. is observed. Even after heating for several hours, the activity is considerably greater than at the ordinary temperature. On cooling, the activity falls, and the normal value is attained at the end of about an hour. This decrease in the activity on cooling was not observed in all the experiments, and the suggestion is made that the samples of emanation which show the phenomenon contain another substance which is very sensitive to rise of temperature. This substance is apparently formed very slowly, for the emanation collected after a period of rest of eighteen weeks showed no decrease in activity on being cooled after exposure to a higher temperature.

H. M. D.

Secondary β -Rays. JOHN A. McCLELLAND (*Proc. Roy. Soc.*, 1908, 80, A, 501—515. Compare Abstr., 1907, ii, 420).—When radiation from radium, consisting of 96% of β -rays and 4% of γ -rays, is allowed to impinge on plates of various metals, the secondary radiation from the metal consists entirely of β -rays.

Although secondary β -rays are emitted in all directions, a very large proportion follows the ordinary law of reflection. The intensity of the reflected beam of β -rays does not vary much when one metal is substituted for another, but the intensity of the true secondary β -radiation, free from reflected rays, depends on the atomic weight of the metal in an even more striking manner than was shown in the previous work. If the amounts of true secondary radiation are plotted against atomic weights, the elements fall into divisions corresponding with the chemical periods. The higher the atomic weight the greater is the amount of β -radiation emitted, and the less the relative importance of the reflected portion.

Experiments were made in which the angle of incidence of the primary radium rays on the plate was 0°, 30°, 45°, 60°, and 75°, whilst the intensity of the emitted radiation was measured at all angles in the plane of incidence up to 75° on each side of the normal to the surface. When the incidence is normal to the surface, the secondary

radiation in any direction is proportional to the cosine of the angle between that direction and the normal. This might be expected from the fact that radiation from an element of volume deep in the plate traverses a thickness of material which is inversely proportional to the cosine of the angle between its direction and the normal.

Secondary radiation is much less from a thin sheet of aluminium than from a thick one, but the reflected portion increases less rapidly than the total radiation when the thickness of the plate is increased. Reflection is not merely a surface action, but goes on at successive layers beneath the surface.

There is good ground for dividing the total secondary radiation into two distinct parts, since true secondary β -rays appear to be more readily absorbed by tinfoil than either reflected or primary β -rays.

In addition to secondary radiation in the plane of incidence, the total radiation from an exposed plate has been measured by placing the plate at the base of an ionisation vessel consisting of three concentric tinfoil hemispheres. The ionisation current from the outer and inner to the middle hemisphere was approximately proportional to the total radiation, however distributed.

Measurements were made with lead, tin, copper, and aluminium, the angles of incidence varying from 10° to 89° to the normal. Given equal amounts of primary radiation falling on the plate, the total secondary radiation appears to vary somewhat with the angle of incidence. The higher the atomic weight the greater the total secondary radiation. With low atomic weights, reflected rays are an important factor, and the author supposes that these are not confined to the plane of incidence.

Reflected β -rays are supposed to actually consist of some of the incident β -particles, whilst true secondary radiation more probably consists of particles expelled from atoms perturbed by the entry of primary rays. The expelled particles may be original constituents of the atom or incident particles previously absorbed by the atom.

R. J. C.

Decay of Radium Emanation when Dissolved in Water. RICHARD B. MOORE (*Proc. Roy. Soc.*, 1908, 80, A, 597—598).—The half-time period for the decay of radium emanation dissolved in water is 3.8 days, practically identical with that observed under ordinary conditions in air. G. S.

Condensation of Radioactive Emanations. E. HENRIOT (*Chem. Zentr.*, 1908, 1, 1515—1516; from *Le Radium*, 1908, 5, 41—46).—With the object of ascertaining whether there is any relationship between the condensation of radium and thorium emanations by cooling and their adsorption by solids when heated, the adsorption of radium emanations by coconut charcoal has been studied. This substance was first treated in the cold with emanation, then heated in a closed vessel to a definite temperature, and the vessel connected with a larger evacuated chamber. The quantity of emanation thereby given up was measured and found to be a regular function of the

temperature; at 18° it is practically zero, and at 350° complete. When actinium emanation was connected by a U-tube to a zinc sulphide screen and the whole apparatus evacuated, no scintillations were produced when the temperature of the U-tube was below -145° , but with an increase of temperature an increased luminosity was observed. In a similar manner, it was found that radium emanation produced luminosity above -150° to -160° . An actinium salt was itself cooled, and the emanation conducted to a condenser by a current of air and measured; it was found that above -140° the quantity of emanation produced increased with the temperature. J. V. E.

Condensation of the Actinium and Thorium Emanations. S. KINOSHITA (*Phil. Mag.*, 1908, [vi], 16, 121—131).—A comparison of the condensation phenomena of the emanations of thorium and actinium has been made by a method similar to that used by Rutherford and Soddy for radium and thorium emanations (compare *ibid.*, 1903, [vi], 5, 361). Actinium emanation begins to condense at -120° , but until the temperature falls to -150° the condensation is incomplete. The temperature at which condensation begins, or at which a given proportion of the emanation remains uncondensed, depends largely on the pressure; it is the same whether the emanation is conveyed by air or by hydrogen.

Experiments on thorium emanation made with the same apparatus show that it condenses at temperatures from $2-3^{\circ}$ higher than the actinium emanation. The influence of pressure on the condensation phenomena is very nearly the same for both. H. M. D.

Emission of Electrons by Heated Metallic Oxides.* FELIX JENTZSCH (*Ber. deut. phys. Ges.*, 1908, 6, 398—400. Compare Deiminger, this vol., ii, 83).—The author has measured the number of electrons emitted by twenty different metallic oxides at high temperatures.

Platinum wires, coated with the oxides, were heated electrically and suspended axially in a brass cylinder between which and the oxide-coated wire a difference of potential was established, and the saturation current was measured. In all cases, the formula deduced by Richardson (*Phil. Trans.*, 1903, A, 201, 516) is satisfied by the experimental data.

Values representing (1) the number of electrons contained in unit volume of the emitting substance, and (2) the work done by an electron in passing through the surface of the active substance, are tabulated for the various oxides examined. The work done by an electron on emission is greater for the oxides of the electropositive metals than for those of the electronegative metals. On the other hand, the number of free electrons in the electropositive metals exceeds that in the electronegative. H. M. D.

Changes of Pressure which Accompany Point Discharge through Hydrogen containing Oxygen and Nitrogen. A. P. CHATTOCK and A. M. TYNDALL (*Phil. Mag.*, 1908, [vi], 16, 24—47).—Experiments have been made to ascertain the molecular complexity of

the ions in point discharge through hydrogen. By discharging from a platinum point against a platinum or palladium plate, the ions appear to be absorbed by the plate, resulting in a diminution of pressure, from which the number of molecules removed from the gas per ion can be calculated when the quantity of electricity passing through the gas during the discharge is known. (The expression "per ion" is to be interpreted as "per hydrogen atom set free in a voltameter placed in series with the discharge vessel.") The pressure changes were measured by means of a sensitive tilting pressure gauge capable of indicating differences of the order of $1 \cdot 10^{-8}$ atmosphere.

In pure hydrogen, the pressure change corresponds with the removal of one molecule per ion. In hydrogen containing 2 to 14% by volume of oxygen, positive point discharge brings about the combination of about 16 molecules of oxygen per ion, whilst negative discharge causes about 25 molecules of oxygen to combine per ion. When the percentage of the oxygen is less than 0.2, the number of molecules which combine in the positive discharge is approximately constant, and equal to about 10 per ion. For negative discharge, the combination increases rapidly when the percentage of oxygen falls below 2, and in hydrogen containing less than 0.01% of oxygen it attains the high value of 110 molecules per ion.

The presence of one part of oxygen in ten million parts of hydrogen can be detected by means of the pressure changes which accompany the point discharge.

When nitrogen is present with oxygen in hydrogen, even in large excess, the combination which takes place is chiefly, and perhaps entirely, between the oxygen and the hydrogen. H. M. D.

Does the Law of the Action of Mass Hold for the Silent Electrical Discharge? MAX LE BLANC and JOHN H. DAVIES (*Zeitsch. Elektrochem.*, 1908, 14, 361—366).—When dry ammonia gas is exposed to the silent discharge at constant temperature and constant current, the rate of decomposition is nearly proportional to the pressure. Temperature has a comparatively small influence on the rate of decomposition; a rise of 100° nearly doubles it. An increase of the current of one-third nearly doubles the rate of decomposition. The presence of excess of hydrogen diminishes the rate of decomposition, whereas nitrogen increases it. The luminosity of the discharge is much increased by nitrogen, but not by hydrogen. The final condition of equilibrium attained is found to be very little affected by the strength of current used. The ratio $[N_2][H_2]^3/[NH_3]^2$ for different mixtures of hydrogen and nitrogen is not even roughly constant. The law of mass action therefore does not hold. Apparently, it is only true when the temperature is so high that the reactions occur under the influence of heat alone. T. E.

Volatilisation of Cathodes in Attenuated Gases. FRANZ FISCHER and OTTO HÄHNEL (*Zeitsch. Elektrochem.*, 1908, 14, 366—367).—The authors have compared the volatilisation of different cathodes with the same current by using two discharge tubes in series. With the same metal and gas, the volatilisation is approximately inversely

proportional to the gas pressure and directly proportional to the square of the current density. The volatilisation in argon and hydrogen is the same; it is less in air than in hydrogen. The order of volatility of the metals is aluminium, iron, nickel, copper, platinum, silver. If the tubes are in parallel, the current passes more readily through argon than hydrogen, and the volatilisation in the argon tube is greater. Kohlschütter and Goldschmidt (this vol., ii, 457) find that different gases favour volatilisation in the order of their atomic weights. This is not in agreement with the present experiments, and is also contradicted by Kohlschütter and Goldschmidt's results when these are calculated for equal quantities of electricity. T. E.

Electrocapillary Measurements by the Method of Large Drops. LÉON G. GOUY (*Compt. rend.*, 1908, 146, 1374—1376).—The present paper deals with absolute measurements by means of a modified capillary electrometer. In order to obtain a rigorously hemispherical drop, the mercury is contained in a glass vessel, optically worked, and of 40 mm. radius. Results are given for solutions of hydrogen sulphate, sodium sulphate, hydrogen chloride, potassium bromide, and potassium iodide. W. O. W.

Determination of the Dielectric Constant of Helium. ERNST HOCHHEIM (*Ber. deut. phys. Ges.*, 1908, 6, 446—448).—The author has measured the dielectric constant of helium by the electrostatic null-method of Hopkinson-Lebedeff. The mean value reduced to 0° and 760 mm. pressure is $D = 1.000074 \pm 0.000004$. If the mean value n of the refractive index of helium is taken from the measurements of Scheel and Schmidt, Ramsay and Travers, and of Rayleigh, the relationship of Maxwell, $D = n^2$, is found to be satisfied. H. M. D.

Electrical Conductivity of Solid Cuprous Iodide. KARL BÄDEKER and E. PAULI (*Physikal. Zeitsch.*, 1908, 9, 431).—The electrical conductivity of cuprous iodide, which is abnormally high for a transparent substance, is found to diminish with time. By subjecting a very thin film of copper to the action of iodine vapour in a suitable apparatus, an initial maximum specific resistance equal to 0.01 ohm. was obtained for the iodide. In an atmosphere saturated with iodine vapour, the conductivity remains unchanged, but falls immediately when the iodine vapour is removed by a current of hydrogen or air. On saturating again with iodine vapour, the original high value of the conductivity is attained, and the transformation can be repeated with the same specimen of cuprous iodide as often as desired. H. M. D.

A Peculiar Type of Electrical Conductivity. KARL BÄDEKER (*Physikal. Zeitsch.*, 1908, 9, 431—433. Compare preceding abstract).—The rise of the electrical conductivity of cuprous iodide which is observed when the substance is brought into contact with saturated iodine vapour or a saturated iodine solution takes place asymptotically; approximately four-fifths of the total increase is observed in the first minute. The increase in the conductivity is accompanied by a slight darkening of the colour and by an increase in weight. The maximum

increase in weight of the substance when in an atmosphere of iodine corresponds with the addition of 0.00333 gram of iodine per gram of cuprous iodide. The proportion of absorbed iodine depends on the temperature and also on the pressure of the iodine vapour, or on the concentration of the iodine in the solution with which the cuprous iodide is in contact. Extremely small iodine vapour pressures or concentrations are, however, very active. The conclusion is drawn that the conductivity induced by the absorption of iodine is metallic in nature; the resistance is the same whether measured by direct or alternating currents, and prolonged passage of a direct current produces no change in the conductivity. The increase in conductivity observed when cuprous iodide is acted on by light is attributed to the separation of traces of iodine.

H. M. D.

Binary Electrodes and Electrochemical Adsorption. LEONOR MICHAELIS (*Zeitsch. Elektrochem.*, 1908, 14, 353-355).—By a binary electrode the author means a substance which sends out positive and negative ions when it dissolves. An acid of small solubility and high molecular weight sends out hydrogen ions and also anions; it may possibly continue to send these out after the solution is saturated; the ions will re-combine, and the undissociated molecules produced will separate out in the solid form. Owing to the different rates of diffusion of the hydrogen ions and the anions, the former will tend to escape from the surface of the solid, leaving it negatively charged. It therefore behaves like a hydrogen electrode, and the difference of potential between it and the solution depends on the concentration of the hydrogen ions in the solution. The addition of an acid diminishes the potential difference, and therefore increases the surface tension of the solid particles. The precipitation of a suspension of mastic by acids is explained in this way. The precipitation by a basic colouring matter, such as methyl-violet, is explained by the formation of a salt on the surface of the mastic particles. This diminishes the tendency to send out hydrogen ions, and so diminishes the potential difference and increases the surface tension. This theory is the opposite of that which explains adsorption as a pure surface effect due to the tendency of all substances to take on the form with the smallest surface tension.

T. E.

Thermodynamics of Liquid Cells. P. HENDERSON (*Zeitsch. physikal. Chem.*, 1908, 63, 325-345. Compare Abstr., 1907, ii, 426).—The formula deduced in the earlier paper (*loc. cit.*) has been tested by measurements of the *P.D.* between equally concentrated solutions containing bivalent ions, such as SO_4^{2-} , Ba, Cd, &c. The agreement between the observed and calculated values is fair. In respect to ease of manipulation, the author's formula is superior to Planck's, and the results which it gives are quite as satisfactory. An extension of the formula to concentrated solutions is deduced, and tested by measurements of the *E.M.F.* of the cell:

Ag, AgCl	Conc. HCl solution	Sat.	AgCl, Ag.
	Sat. PbCl_2 solution	PbCl_2 solution	

J. C. P.

Change of Free Energy Accompanying the Formation of Some Fused Salts of the Heavy Metals. RICHARD LORENZ and M. G. Fox (*Zeitsch. physikal. Chem.*, 1908, 63, 169—120).

—The authors describe a form of chlorine or bromine electrode suitable for use at high temperatures, consisting of a hollow carbon tube kept charged with the halogen, and show that this electrode is reversible. The variation of *E.M.F.* with temperature has been determined for a number of cells containing fused salts, and the results are represented by the following formulæ: in these e_{AB} means the *E.M.F.* of the cell $A | AB | B$, AB being the fused salt formed from the elements A and B .

$e_{PbCl_2} = 1.263 - 0.000679 (t - 498^\circ)$ for the temperature-interval $498-660^\circ$; $e_{CaBr_2} = 1.258 - 0.000750 (t - 560^\circ)$, valid between 560° and 740° ; $e_{PbBr_2} = 1.0945 - 0.000714 (t - 367^\circ)$, valid between 367° and 640° ; $e_{CaBr_2} = 1.045 - 0.000742 (t - 580^\circ)$, valid between 580° and 720° .

J. C. P.

Thermodynamics of Cells with Fused Electrolytes. RICHARD LORENZ and M. G. Fox (*Zeitsch. physikal. Chem.*, 1908, 63, 121—125. Compare preceding abstract).—The Gibbs-Helmholtz formula is applied to the cells referred to in the preceding abstract, and the heats of formation of lead chloride and bromide and cadmium chloride and bromide are calculated. The values so found for the four salts are respectively 82.4, 71.5, 86.8, and 77.3 Cal. These figures represent the heats of formation at constant pressure in the temperature-intervals recorded in the previous abstract. So far as comparison is possible, the agreement with the values deduced thermochemically is fair.

J. C. P.

Differences of Potential at the Contact of Two Electrolytes. Nernst's Theory. J. GUYOT (*J. Chim. Phys.*, 1908, 6, 424—491).—Although the general formulæ for the potential difference at the contact of two electrolytes have not yet been obtained, it is shown theoretically that the calculation is not only possible for binary electrolytes with univalent ions (Nernst, Planck), but also for any two electrolytes of the same type (for example, $BaCl_2$, $CaCl_2$), as well as for electrolytes with a common ion when the total ionic concentration is the same for the two solutions. Direct experimental verification of the formulæ is not possible, owing to the fact that no single potential difference is known with accuracy; in particular, it is pointed out that the Helmholtz-Ostwald method for determining single potential differences, depending on electrocapillary phenomena, is not trustworthy.

Measurements have therefore been made with "liquid chains" in which two solutions are in contact with each other and with mercury electrodes, forming cells of the type $M S_1 S_2 M$. The total *E.M.F.* of such a cell is the algebraic sum of the potential differences at the two junctions metal-solutions, and that at the junction of the two solutions $S_1 S_2$. As the former can be calculated for electrodes of the same metal by the usual formula $E = RT/nF \log p_1/p_2$, the *E.M.F.* $S_1 S_2$ is readily obtained. For solutions of salts of the same type, measurements were made with alkali sulphates against sulphuric acid

and against each other, and for solutions of salts of different types such couples as $\text{HCl}|\text{BaCl}_2$, $\text{H}_2\text{SO}_4|\text{CuSO}_4$, and $\text{Na}_2\text{SO}_4|\text{ZnSO}_4$ were used. A few measurements were also made with liquid chains with identical extremities, for example,

$0.1\text{N}\text{K}_2\text{SO}_4|0.2\text{N}\text{Li}_2\text{SO}_4$ and $0.02\text{N}\text{H}_2\text{SO}_4|0.1\text{N}\text{K}_2\text{SO}_4$, the *E.M.F.*'s at the junction metal|solution being thus eliminated. In all cases, the observed and calculated values were in satisfactory agreement. G. S.

A Method for the Calculation of Ionic Concentrations from Measurements of Potential in Concentration Cells. WARREN KENDALL LEWIS (*Zeitsch. physikal. Chem.*, 1908, 63, 171—176).—A method is given for calculating the dissociation of an electrolyte from potential measurements in concentration cells. Applied to the experimental determinations of Cumming with silver nitrate (this vol., ii, 253), very close agreement is obtained. New determinations with lead nitrate and chlorate are also given, the value for the normal lead electrode obtained being 0.402. The advantage of the method in the case of multivalent ions is that it is unnecessary to make any assumption as to dissociation in successive stages. C. H. D.

Electrochemical Equivalent of Silver, Especially in Reference to the So-Called Anode Liquid. FRIEDRICH KOHLRAUSCH (*Ann. Physik*, 1908, [iv], 26, 580—596).—The author has made experiments to ascertain whether the value obtained for the electrochemical equivalent of silver by F. and W. Kohlrausch in 1881, and 1883, requires correction in the light of recent researches on the properties of the anode-liquid. According to these, oxidation products are formed in the solution at the anode, and this leads to inaccurate values for the equivalent. Using the original pieces of apparatus and duplicates of these, the new experiments show that the arrangement of the electrodes is such that the abnormal properties of the anode-liquid do not exert any influence on the result obtained. The correction which might be applied to the value 0.01183 given by the older experiments is at any rate less than 0.002%. H. M. D.

A Lecture Voltameter. R. PIRONI (*Nuovo Cim.*, 1908, [v], 15, 426—428).—The voltameter is of the Hofmann pattern, but the three tubes are of equal diameter and in the same plane. Each is fitted with an electrode, and the centre tube also has an outlet tube and tap at the lower end. In the electrolysis of water, the central electrode may be made the anode, and the two outer ones cathodes; the volume of gas collected in each tube is then equal. The application of the voltameter to polarisation experiments is also described. C. H. D.

Relation between the Ionising Power and the Dielectric Constants of Solvents. HERBERT N. MCCOY (*J. Amer. Chem. Soc.*, 1908, 30, 1074—1077).—Walden has shown (*Abstr.*, 1906, ii, 149) that when solutions of an electrolyte in various solvents have the same degree of dissociation, the product of the dielectric constant and the

cube root of the dilution for such solutions is a constant, or $\epsilon\sqrt[3]{V} = \text{const.}$ Kohlrausch's equation $\Lambda = \Lambda_\infty - k\sqrt[3]{C}$, where Λ is the equivalent conductivity at concentration C , Λ_∞ the conductivity at infinite dilution, and k is a constant, may be written $\Lambda/\Lambda_\infty = 1 - k/\Lambda_\infty\sqrt[3]{C}$ or $\alpha = 1 - K\sqrt[3]{C}$ (1), where the degree of ionisation $\alpha = \Lambda/\Lambda_\infty$ and $k/\Lambda_\infty = K$, a constant. From equation (1) the expression $K = (1 - \alpha)\sqrt[3]{V}$ (2) is obtained. The data for sodium chloride are tabulated, in which the values of α are calculated by equation (1). Similar calculations have been made for about thirty other salts. The differences between the observed and calculated values of α do not exceed the probable experimental error. It is shown that equation (1) applies fairly accurately to many solutions in inorganic solvents, and the values of $K = (1 - \alpha)\sqrt[3]{V}$, ϵ , and $K\epsilon$ for tetraethylammonium iodide in various solvents are calculated from Walden's data. The results are also given for potassium iodide in water, ethyl alcohol, and acetonitrile, and for lithium nitrate in water, methyl alcohol, and 50% methyl alcohol. In the case of potassium iodide, the value of $K\epsilon$ is nearly the same for ethyl alcohol as for water, but is abnormally large in acetonitrile. For lithium nitrate, $K\epsilon$ has the same value for water and for methyl alcohol.

E. G.

Electrolytic Rectification of Alternating Currents. GUNTHER SCHULZE (*Zeitsch. Elektrochem.*, 1908, 14, 333—347).—The author's experiments with direct current (*Ann. Physik*, 1906, 21, 929; 1907, 22, 543; 23, 226; 24, 43; 1908, 25, 775) have shown that the active electrode in an electrolytic rectifier is covered with a porous, non-conducting skin. The pores next to the metal are filled with gas, and the remainder are full of the electrolyte. When the electrode is cathode, negative corpuscles pass from it through the gas layer to the electrolyte without much resistance; when the electrode is anode, however, the carriers of the current in the electrolyte are anions which cannot pass through the gas layer. In the anode direction, the gas layer has a resistance of the order of 500 ohms per sq. decimetre; it also has a capacity of the order of 5 microfarads per sq. decimetre, and with alternating current of 50 periods per second, this allows the same current to pass as a resistance of 640 ohms. The resistance of the electrolyte is negligible compared with this, so that the current in the anode direction is conditioned by the resistance and capacity of the gas layer. In the cathode direction, the resistance of the gas layer and of the electrolyte are each of the order of 10 ohms per sq. decimetre; the capacity of the gas layer is therefore negligible. The theoretical shape of the current and *E.M.F.* curves are deduced from these considerations. A large number of curves are taken by means of an oscillograph, using electrodes of all the active metals known. The curves agree well with the theoretical forms. As a criterion of the relative values of the cells, the ratio of their apparent resistances in the cathode and anode directions is used. With aluminium in solutions of salts of potassium or sodium, the ratio is small, but the active layer soon breaks down. The danger of breakdown is smaller with ammonium salts, but the ratio is larger. Breakdown is never observed with

tantalum, but the ratio is much too large; its ability to resist *E.M.F.*'s of 1000 volts is of no use in practice, because of the very dilute solutions required. Magnesium has a very small ratio of resistances, but the active layer is very sensitive to rise of temperature. Since the liability to breakdown and a small ratio of resistances appear to be both due to the same cause (solubility of the solid skin in the electrolyte), it is improbable that a satisfactory electrolytic rectifier will be discovered.

T. E.

Theory of Dulong and Petit's Law. II. FRANZ RICHARZ (*Zeitsch. anorg. Chem.*, 1908, 59, 146—160. Compare this vol., ii, 562).—A theoretical discussion of the causes which lead to deviations from Dulong and Petit's law. The author's theory, which requires that the product of the atomic weight and the specific heat at constant volume should be equal to 6.012, cannot be tested directly by ordinary experimental data. That elements of small atomic weight and small atomic volume represent exceptions is anticipated by the author's theory. In accordance with this, it is also found that of two allotropic modifications, the one with the smaller atomic volume has the smaller specific heat.

H. M. D.

Equation of Condition for Metals. MAX THIESEN (*Ber. deut. phys. Ges.*, 1908, 6, 410—415, 415—417. Compare Grüneisen, this vol., ii, 563).—A discussion of conclusions regarding the equation of condition, which may be drawn from the relationship pointed out by Grüneisen, that for a number of metals the quotient of the coefficient of expansion by the specific heat is almost independent of the temperature. The significance of this relationship depends on whether the equation of condition for a solid, crystalline substance is different from the equation for the same substance in the liquid condition or in another crystalline form, or whether the same equation of condition holds for all forms of the substance. In the first case, the relationship may be strictly true for certain crystalline forms, but in the second case the relationship can only be regarded as approximately valid for a finite portion of the curve of condition.

H. M. D.

Specific Heat and Molecular Magnetic Field of Ferromagnetic Substances. PIERRE WEISS and PAUL N. BECK (*Arch. Sci. phys. nat.*, 1908, iv, 25, 529—548).—The energy transfer when ferromagnetic substances are magnetised or demagnetised by alterations in temperature is of the same order as the energy required to effect the temperature change itself.

The authors endeavour to show that the anomalies exhibited by the specific heats of magnetic metals (Pionchon, *Abstr.*, 1887, 201) can be quantitatively explained as due to variations in the magnetic energy content.

Assuming each molecule to be a magnet producing lines of force, the energy of complete demagnetisation of iron is calculated to be 16.8 cal. per gram at 20°, becoming less as the temperature rises, and finally disappearing at 753°, at which temperature the iron loses its magnetic properties. The energy of demagnetisation of nickel varies

from 4.3 cal. at 22.9° to zero at 376°, whilst the corresponding values for magnetite are 14.4 cal. at 15.2° and zero at 588°.

At the ordinary temperature the magnetic phenomena should account for one-twentieth of the specific heat of iron, whilst in the neighbourhood of 753° the proportion would be as much as 43%. Thus the specific heat of iron undergoes an abrupt diminution at 753°.

Calorimetric measurements of the specific heat of iron, nickel, and magnetite over a wide range of temperatures show striking agreement with the results calculated from the magnetic properties. The specific heat of iron alters by 0.112 at 758°, whereas the figures calculated from the magnetic properties are 0.136 at 753°. Values for nickel and magnetite are in still better agreement with the theory.

R. J. C.

The Solid State. W. A. KURATOFF (*J. Chim. Phys.*, 1908, 6, 337—354).—The melting points and equal fractions of the absolute melting points are to be regarded as corresponding temperatures for solids. It is shown by an examination of the available experimental data that at such temperatures the electrical conductivities, divided by the conductivities at the melting points, are equal for different metals, and that both electrical and thermal conductivity are periodic functions of the atomic weight. At corresponding temperatures, the law of Dulong and Petit holds rigorously, even for boron, carbon, and silicon. The evidence indicates that the molecules of solid metals are monatomic, those of solid non-metals being more complex. The molecules of sulphides, oxides, and other compounds with metallic lustre are non-associated.

C. H. D.

The Heat-contents of Binary Systems. GUSTAV TAMMANN (*Zeitsch. physikal. Chem.*, 1908, 63, 129—140).—The thermal equilibrium of binary mixtures may be represented advantageously by means of a three-dimensional model. The ordinary temperature-concentration diagram is used as the base of the model, and perpendiculars are then erected, the heights of which are proportional to the heat-content of unit mass, the upper surfaces then being constructed by means of these perpendiculars. Sections perpendicular to the concentration axis give the variation of heat-content with temperature for a given composition. Photographs of a number of such models, with the corresponding temperature-concentration diagrams, are given for each of the cases discussed by Roozeboom.

In order to construct the model, cooling curves of the mixtures must be taken under similar cooling conditions, and the duration of each arrest determined, as in Tammann's method of thermal analysis (*Abstr.*, 1904, 113).

C. H. D.

Correction of the Ideal Melting-point Curves of Binary Alloys. DOMENICO MAZZOTTO (*Nuovo Cim.*, 1908, [7], 15, 401—422).—The author applies two corrections to the ideal melting point curve, one depending on the heat of mixture, and the other on the association of the dissolved metal. The data for the former correction are obtained from the author's determinations (*Rend. R. Ist. Lombardo*,

1888, [ia], 18, 165), and those for the latter from the atomic depressions measured by Heycock and Neville (Trans., 1889, 55, 666; 1890, 57, 376, 656, 1892, 61, 888; 1894, 65, 31; 1897, 71, 383; Abstr., 1897, ii, 245). The application of these corrections to the melting points of alloys of bismuth and tin, lead and tin, and lead and bismuth, gives curves approximating very closely to the ideal curves. The method fails when the two components form a solid solution, as in the case of tin dissolved in zinc, or when chemical combination takes place, as in lead amalgams. The following coefficients of polymerisation were determined: Bi in Sn, 1.25; Bi in Pb, 2.2; Sn in Pb, 3.8; Zn in Sn, 1.15.

C. H. D.

A Cryoscope. M. C. DEKHUYZEN (*Biochem. Zeitsch.*, 1908, 11, 345—381).—The true freezing point of a solution can be expressed by the equation $t_w = t_s + k_a/K_E(t_s - t_c)$, where t_w is the true freezing point, t_s the apparent (actually read) freezing point, and t_c the "convergence temperature," that is, the temperature which the solution will attain when congelation does not take place. k_a is a constant depending on the rate at which the equilibrium of temperature between the freezing vessel and cooling bath is attained. K_E is a number, by means of which the rate can be calculated at which the ice in the supercooled liquid is formed or dissolved. The above formula is due to Nernst and Abegg. The constant k_a can be directly determined, the equation $-dt/dz = k_a(t - t_c)$, where z represents time, denoting the rate of temperature change of the liquid. From this equation,

$$k_a = 1/(z_2 - z_1) \cdot \log. nat. (t_1 - t_c)/(t_2 - t_c),$$

where t_c represents the temperature of the cooling mixture. To determine K_E , the following formula was evolved:

$$dt/dz = K_E(t_w - t_s) - k_a(t_s - t_c).$$

A practically constant cooling bath can be obtained by applying the principles that ice and salt solution attain temperature equilibrium with very small velocity if the surface of the ice and the stirring of the liquid be reduced to the lowest possible limits.

The apparatus employed consists of an inner cooling vessel with ground flange, fitted into a somewhat large cooling vessel, also with ground flange; the two ground surfaces are clamped together. This is covered with an ebonite plate, into which fit two tubes, one of which contains mercury, for quick cooling, and the other tube is a Dewar vessel, formed from two concentric test-tubes with an evacuated space between. A special arrangement made for transferring the vessel containing the liquid under investigation (with the Beckmann thermometer) from the quick-cooling to the Dewar tube is described, and also the methods for determining the values of k_a and K_E .

S. B. S.

Boiling and Freezing Points of Concentrated Aqueous Solutions and the Question of the Hydration of the Solute. SAMUEL M. JOHNSTON (*Trans. Roy. Soc. Edin.*, 1908, 45, Part 4, 855—884. Compare Abstr., 1906, ii, 9).—Boiling point, freezing point, and electrical conductivity data are recorded for concentrated

aqueous solutions of a number of electrolytes. The conductivity measurements were made at 0° and 99.4°.

In general, the rise of the boiling point produced by one gram equivalent has a minimum value at a concentration of 0.5 to 1.0 gram equivalent per litre. For higher concentrations than that corresponding with this minimum, the rate of increase of the equivalent boiling point elevation gradually diminishes, and in certain cases a maximum can be observed.

From a comparison of curves which represent the variation of μ/μ_0 with the concentration of the dissolved electrolyte, the conclusion is drawn that the degree of ionisation is greater at 0° than at 100° in the case of dilute solutions, whereas concentrated solutions are more dissociated at the higher temperature.

Assuming that the ionisation can be obtained from conductivity data, and that the elevation of the boiling point (or depression of the freezing point) produced by a gram molecule or gram ion is independent of the concentration of the solution, the experimental data are used to calculate the degree of hydration of the dissolved electrolyte on the assumptions (1) that molecules and ions are hydrated; (2) that the ions only are hydrated, and (3) that the undissociated molecules only are hydrated. The fact that the values obtained on the first assumption are in some cases constant for a series of concentrations is regarded as evidence of hydration of both the undissociated molecules and the ions. For other electrolytes, hydration of the molecules or of the ions alone is assumed.

H. M. D.

Theoretical Determination of the Vapour Pressure of Solid and Liquid Carbon Dioxide. E. FALCK (*Physikal. Zeitsch.*, 1908, 9, 433—437).—The validity of Nernst's thermodynamic formula for the variation of vapour pressure with temperature has been examined for liquid carbon dioxide between -10° and -60° and for the solid between -60° and -154° . The agreement between the calculated and experimental values is very good, except in the neighbourhood of -100° to -130° . A similar deviation for an intermediate range of temperature was found by Naumann in the case of iodine.

The molecular heats of liquid and solid carbon dioxide are given by the formulae $C_l = 3.8 + 0.077T$ and $C_s = 3.8 + 0.032T$ respectively. At all temperatures above absolute zero, liquid carbon dioxide has therefore the greater specific heat.

The free energy and the heat change for the passage of solid carbon dioxide into the liquid form at various temperatures are calculated. The curves representing these values are symmetrical and tangential to a straight line parallel to the axis of temperature.

H. M. D.

Mutual Action of Dissolved Substances as Deduced from their Vapour Pressures. ADAM WRÓCZYŃSKI (*J. Chim. Phys.*, 1908, 6, 500—504).—Remarks on Konowaloff's recent papers (*Abstr.*, 1907, ii, 334, 602). It is shown that several of Konowaloff's formulae can be deduced from the general Duhem-Margules formula for the vapour pressures of binary mixtures with the help of Raoult's law. It follows that, contrary to Konowaloff's view, there is no proof of

chemical combination under the conditions of experiment in many of the binary mixtures studied by that author. G. S.

Vaporisation I. HANNS VON JÜRTNER (*Zeitsch. physikal. Chem.*, 1908, 63, 355—366. Compare Abstr., 1906, ii, 522; 1907, ii, 742).—The values of f calculated by the empirical equation $f = f_0 - a\theta + b_1(1-\theta)$ (see *loc. cit.*) are in the neighbourhood of the critical temperature greater than those derived directly from observation. The author now shows that when the third term on the right hand side of the foregoing formula is multiplied by the factor $1 - \theta/[e(1-\theta) + 1]$, where e is a constant, a better agreement is secured, as shown by figures for fluorobenzene, carbon dioxide, and ammonia.

By combining this modified equation with the Clapeyron-Clausius formula, an expression is obtained for the latent heat of vaporisation.

According to Mathias, $(D_l + D_v)/2D_k = 2 - \theta$, where D_l and D_v are the densities of liquid and saturated vapour respectively, and D_k is the critical density. The agreement between the experimental figures and the values calculated by this formula is in general very good, but, according to the author, the expression $1 + a'(1-\theta)$ on the right-hand side, where a' is a constant for each substance, gives even better results, as shown by figures for fluorobenzene and ammonia. A formula is also developed for calculating the difference between the densities of liquid and saturated vapour, and is tested with satisfactory results by the available data for fluorobenzene and ammonia. Formulae are further deduced for calculating the densities and volumes of liquid and saturated vapour in terms of θ and the various constants quoted above. J. C. P.

Sources of Error in the Ebullioscopic Method and Attempts to Remove Them. ERNST BECKMANN [With OTTO LIESCHE and THEODOR KLOPPER] (*Zeitsch. physikal. Chem.*, 1908, 63, 177—215).—An elaborate series of experiments has been made to determine the sources of possible error in ebullioscopic determinations. The influence of the external temperature is discussed, and is shown to be least for concentrated solutions; it is less than in the case of cryoscopic experiments. Direct electrical heating by means of a thin platinum spiral is very suitable for non-electrolytes, especially when the boiling point of the solvent is high. Electrolytes give abnormal results, even when an alternating current of high frequency is employed.

A method is described by which satisfactory measurements can be obtained with the bulb of the thermometer immersed only in vapour. The device employed keeps the bulb of the thermometer free from liquid, a layer of boiling liquid forming a jacket round the vapour space. In another form of apparatus, the bulb is immersed in liquid free from vapour, jacketed with the vapour from the same solution.

The influence of the nature and quantity of filling material (garnets or platinum tetrahedra) is also discussed. U. H. D.

Apparatus for Fractional Distillation under Reduced Pressure. WILHELM STEINKOPF (*Bull. Soc. chim.*, 1908, [iv], 3, 763—764).—Attention is directed to the author's apparatus for this

purpose (*Chem. Zeit.*, 1902, 26, 407), which resembles Delepine's (this vol., ii, 461), but differs in having the cylindrical receiver closed by a rubber stopper, through which the distributor, provided with a side tube for attachment to a pump, passes.

T. A. H.

Modification of the Platinum Vessel of the Berthelot-Mahler Bomb. EDUARD TÓTH (*Chem. Zeit.*, 1908, 32, 608).—So as to minimise the wear-and-tear of the pastille, and to facilitate the arrangement of the fuse-thread, it is suggested that the bottom of the platinum vessel should be hollowed out in a pod-like form so that the fuse-thread can be introduced after weighing without disturbing the pastille.

J. V. E.

Heat of Neutralisation of Acetic and Benzoic Acids by Aniline in Benzene Solution. LÉO VIGNON and ÉMILEX (*Compt. rend.*, 1908, 146, 1316—1318).—The molecular heats of dissolution of acetic acid, benzoic acid, and aniline, in benzene at $M/4$ dilution are -0.51 Cal., -3.54 Cal., and -1.09 Cal. respectively. When equal volumes of $M/4$ solutions of acetic acid and aniline are mixed, a fall of temperature (0.054°) is observed corresponding with an absorption of -0.16 Cal. per molecule. On the other hand, the formation of aniline acetate directly from the acid and base results in the development of heat, whilst the heat of dissolution of aniline acetate in benzene ($M/8$ dilution) is -3.63 Cal., from which the value $+1.87$ Cal. is deduced for the molecular heat of combination of acetic acid and aniline.

Similarly, by mixing equal volumes (200 c.c.) of $M/4$ solution of benzoic acid and aniline in benzene, a very slight elevation in temperature (0.024°) is produced, corresponding with a development of 0.08 Cal. per molecule. Aniline benzoate, however, has a heat of dissolution of -9.4 Cal. at $M/8$ dilution in benzene, giving the value $+4.77$ Cal. for the heat of formation.

Determinations of the molecular weights of aniline acetate and benzoate by the cryoscopic method give the values 111 and 151—153, which more nearly agree with those calculated for mixtures of the acid and base than for the salts.

The conclusions are drawn that aniline does not combine with acetic and benzoic acids in benzene solution, and that aniline acetate and benzoate are dissociated by dissolution in benzene.

E. H.

Heat of Neutralisation of Picric Acid by Different Aromatic Bases in Benzene Solution. LÉO VIGNON and ÉMILEX (*Compt. rend.*, 1908, 147, 67—69).—Picric acid differs from benzoic and acetic acids (preceding abstract) in that it combines with aromatic bases in benzene solution.

The molecular heat of dissolution of picric acid in benzene at 20° and $M/8$ dilution is -3.8 Cal. The following are the heats of neutralisation of picric acid by various bases, and the characters of the salts formed. By aniline, $+14.75$ Cal.; aniline picrate forms small, yellow crystals, of which 100 parts of water dissolve 0.54 part and 100 parts of benzene 0.078 part at 22° . *o*-Toluidine, $+16.45$ Cal.;

o-toluidine picrate is precipitated as orange-yellow flocks, which quickly change into yellowish-white crystals. *m*-Toluidine, +15.98 Cal.; *p*-toluidine, +18.15 Cal.; *m*- and *p*-toluidine picrates form clear, yellow crystals. Methylamine, +11.07 Cal. (solid salt); methylamine picrate forms a golden-yellow, crystalline powder, m. p. 134°. Dimethylaniline, +14.1 Cal. (solid salt); dimethylaniline picrate is a granular, yellow powder, m. p. 142°. Ethylaniline, +12.6 Cal. (solid salt); ethylaniline picrate forms a clear yellow, crystalline powder, m. p. 132°. Dimethylo-toluidine, +9.45 Cal. (salt dissolved); the golden-yellow solution, after twenty-four hours' standing, deposits clear yellow crystals of dimethyl-*o*-toluidine picrate, m. p. 116–117°, of which 100 parts of benzene at 25° dissolve 1.35 parts. Phenylhydrazine, +19.03 Cal. (solid salt); phenylhydrazine picrate forms a bright yellow powder, m. p. 148–149°.

The molecular heat of dissolution of *o*-nitroaniline at 22° and *M*/8 dilution is -5.51 Cal., and its heat of neutralisation by picric acid is -0.35 Cal. The heat of dissolution of *o*-nitroaniline picrate, a brick-red, crystalline powder, in benzene at 22° and *M*/16 dilution is -8.40 Cal., whence the heat of formation in benzene solution is -1.2 Cal. A cryoscopic determination of the molecular weight in benzene solution also shows that no combination has taken place.

These results are an example of salt formation without ionisation. The electrical conductivity of the solutions either before, during, or after admixture is inappreciable.

Benzene solutions of phenol, nitrobenzene, and *m*-dinitrobenzene do not react with a benzene solution of *p*-toluidine.

The conclusions are drawn that (1) salt-formation in benzene differs from that in water, (2) that benzene having no appreciable ionising power is particularly useful for the thermal study of the formation of certain salts, (3) that the presence of several nitro-groups in the benzene nucleus greatly intensifies the acidic power of the hydroxyl group, and (4) that the acidity of picric acid becomes zero towards certain bases, such as *o*-nitroaniline.

Other acids, such as trichloroacetic acid, in which the acidic character is intensified by the presence of the three chlorine atoms, behave similarly to picric acid.

E. H.

Heats of Solution of the Three Forms of Lactose. C. S. HUDSON and F. C. BROWN (*J. Amer. Chem. Soc.*, 1908, 30, 960–971).—Lactose can be crystallised from solution in two forms, the monohydrate and the β -anhydrous modification. When the hydrate is heated at 125°, it is converted into the α -anhydrous form. Hudson (Abstr., 1904, i, 974) has determined the rate at which equilibrium is established between the hydrate and the β -modification, and the proportions of the two forms finally present. A study has now been made of the heats of solution of the three forms of lactose, keeping in view the fact that the solution of any one form is complicated by a second heat effect due to the change into the stable mixture of hydrate and β form. The following terms are employed: The "initial heat of solution" is the heat produced when any form of the sugar is dissolved under such conditions that the change into the

mixture of hydrate and β -form is greatly retarded. The "final heat of solution" is the total heat developed when any form of the sugar dissolves to yield a solution containing the stable mixture. The "heat of passage" of one form into the other is the heat produced when a given quantity of one form changes in solution into an equivalent quantity of the other. The final heat of solution is thus the sum of the initial heat of solution and the heat of passage. The following results have been obtained by means of calorimetric measurements.

The initial heats of solution in gram-calories are: hydrate, -12.0 ; α -form, $+7.3$; β -form, -2.3 . The final heats of solution are: hydrate, -11.4 ; α -form, $+7.9$; β -form, -2.7 . The heats of passage to the β -form are: hydrate, $+1.0$; α -form, $+1.0$. The equality of the heats of passage of the hydrate and the α -form support the view that in solution the α -form instantly changes into the hydrate, which is then slowly converted into the β -form. The initial heat of solution of the hydrate increases about 0.1 gram-cal. per degree rise in temperature. On diluting strong lactose solutions (0.5 molal), a slight development of heat occurs, but the heat of solution is independent of the concentration when this is less than about 0.3 molal. The pure β -form has been prepared, and has $D_{20}^{20} 1.59$, whilst the hydrate has $D_{20}^{20} 1.54$. The thermochemical data now obtained show that the crystalline substance precipitated from aqueous solutions of lactose by alcohol and ether is a mixture of the hydrate and β -modification, the two forms being present in approximately the same proportions in which they occur in stable solutions. Observations of the rotatory power of stable solutions of the sugar indicate that the hydration is slightly increased with rise of temperature from 0° to 100° . The final heat of solution of the hydrate, calculated from the solubilities at 15° and 25° , is -11.5 , which agrees closely with the calorimetric determination at 20° .

E. G.

New Instrument for Reducing Gas Volumes to Standard Conditions. GRANT T. DAVIS (*J. Amer. Chem. Soc.*, 1908, 30, 971-973).—An apparatus is described for so adjusting the pressure on a gas that its volume is reduced to that which it would occupy under standard conditions of temperature and pressure, calculation being thus avoided. The pressure is applied by means of a column of water, and the method is therefore only suitable for gases which can be collected over water. For details, the description and diagram in the original must be consulted.

E. G.

Orthobaric Densities of Homologous Liquids. G. TERGAZARIAN (*J. Chim. Phys.*, 1908, 6, 492-499).—From the author's determinations of the densities and critical temperatures of acetonitrile and propionitrile, and from the corresponding determinations of Young for pentane, isopentane, hexane, heptane, and octane, it is shown that the difference between the temperatures of equal densities for two homologous liquids is equal to the difference of the critical temperatures of the same liquids. Hence, if the density curve (liquid) and the critical temperature of a single member of the

series is known, the density curve and critical temperature of all the other members can be calculated, if the density at a single temperature is known in each case.

The rule in question does not hold for the esters and alcohols studied by Young and Thomas (Trans., 1893, 63, 1191). G. S.

The Unit-Stere Theory: Demonstration of a Natural Relation between the Volumes of the Atoms in Compounds under Corresponding Conditions and that of Combined Hydrogen. II. GERVAISE LE BAS (*Phil. Mag.*, 1908, [vi], 16, 60-92. Compare Abstr., 1907, ii, 754).—The volume relationships of carbon and hydrogen in the liquid hydrocarbons of the olefine and acetylene series, and in aromatic and hydroaromatic compounds, have been examined in the light of the theory put forward in the earlier paper on the basis of data for the liquid normal paraffins.

At the melting point and at temperatures equally removed therefrom, the molecular volumes of the olefines may be represented by the expression: molecular volume $C_nH_{2n} = 6nS - 2.62 = WS - (=)$. Similarly, the molecular volumes of the acetylenes are given by: molecular volume $C_nH_{2n-2} = 6nS - 2S - 3 = WS - (\equiv)$. In these expressions, S is the value of the unit-stere = 2.97, W is the total number of valencies of the atoms in the hydrocarbon molecules, and the bracketed symbols represent the volume values corresponding with the unsaturated linkages.

At the boiling point, the molecular volumes of the olefines and acetylenes are given by the formulae: molecular volume $C_nH_{2n} = 6nS$ and molecular volume $C_nH_{2n-2} = 6nS - 2S$ respectively. The value of S is approximately 3.7, but appears to vary slightly from one compound to another.

The data for aromatic compounds indicate that the atomic volumes in the nuclei are always less than the volumes of the same atoms in straight-chain molecules. The relative volumes of atoms are, however, the same in both cases. The atoms in aliphatic side-chains of aromatic compounds have the same volume as in the paraffins.

In the case of benzene and its homologues, it is shown that the critical coefficients are also subject to the valency law. H. M. D.

Torsional Elasticity of Liquids. L. LAUER and GUSTAV TAMMANN (*Zeitsch. physikal. Chem.*, 1908, 63, 141-150).—An apparatus is described by means of which a known torque of short duration could be applied to a glass sphere immersed in the liquid to be examined. The duration of the impulse varied from 0.0000163 to 0.01956 second, and was regulated and measured by means of a Helmholtz pendulum. In other experiments, a steel rod of elliptical section was substituted for the glass sphere.

The liquids investigated were water, glycerol, and undercooled betol containing 1.5% sucrose. The last two gave positive indications of torsional elasticity, increasing with falling temperature. The temperature at which elasticity becomes marked is independent of the duration of the impulse, and almost independent of the moment of torsion. This

temperature is 63° for glycerol and 41° for betol. Water does not exhibit any elasticity above its melting point. C. H. D.

Weight of a Falling Drop and the Laws of Tate. Determination of Molecular Weights and Critical Temperatures of Liquids by the Aid of Drop Weights. II. J. LIVINGSTON R. MORGAN and ERIC HIGGINS (*J. Amer. Chem. Soc.*, 1908, 30, 1055—1068).—Morgan and Stevenson (this vol., ii, 356) have shown that the weight of a drop of liquid falling from the properly cut end of a glass capillary tube is proportional to the surface tension of the liquid, and can be employed for calculating the molecular weight and critical temperature.

In the present paper, an account is given of experiments which have been carried out with a bevelled tip similar to that used by Morgan and Stevenson, but attached to a burette of smaller diameter than that previously employed. The drop weights of carbon tetrachloride and the liquids studied in the earlier work have been determined at or near the temperatures at which their surface tensions have been measured by the rise of the liquids in a capillary tube. The results are tabulated. They confirm those obtained previously, and show that, for the determination of relative surface tensions, the drop-weight method is more accurate than the ordinary method depending on capillary rise, and, also, that the molecular coefficient of drop weight is a true constant. The drop-weight method is therefore the most accurate available for the determination of molecular weights, except that for permanent gases, which is based on the density. It is also shown that critical temperatures can be more readily and accurately calculated from drop weights than from capillary rise. E. G.

New Formulæ Correlating the Various Constants for Non-associated Liquids. ERIC HIGGINS (*J. Amer. Chem. Soc.*, 1908, 30, 1069—1074).—Morgan and Stevenson (this vol., ii, 356) and Morgan and Higgins (preceding abstract) have described a method of determining the volumes (and hence the weights) of drops of non-associated liquids delivered from the specially cut end of a capillary tube.

Since the drop volume is proportional to the surface tension, it is shown that $vM/T = K$, where M is the molecular weight of the substance in the liquid state, v the drop volume, and T the absolute temperature of the b. p. By means of these drop-volume constants of certain non-associated liquids (benzene, pyridine, chlorobenzene, aniline, and quinoline), the following can be calculated from a knowledge of the b. p., molecular weight, and density: the surface tension, critical temperature and pressure, vapour pressure at any temperature, latent heat of evaporation, and the value of a and b in van der Waals' equation. It is also shown that the drop weight and b. p. of a liquid enable its molecular weight to be ascertained, and hence all the constants already enumerated can be calculated. E. G.

Viscosity of Non-aqueous Solutions of Potassium Iodide. FREDERICK H. GETMAN (*J. Amer. Chem. Soc.*, 1908, 30, 1077—1084).—In earlier papers (Abstr., 1907, ii, 744; this vol., ii, 464), it has

been suggested that the cations of an electrolyte lower the viscosity of a solvent, whilst the anions and non-ionised molecules increase it. It has been considered desirable to test this hypothesis by working with non-aqueous solutions in which the degree of ionisation is less than in water. For this purpose, a study has been made of solutions of potassium iodide in methyl and ethyl alcohols, ethylene glycol, glycerol, furfuraldehyde, acetone, and pyridine. The density of the solutions at 25°/4°, the absolute viscosity, and the ratio of the absolute viscosity of the solutions to that of the solvents are recorded.

The results show that all the solutions, except that in glycerol, exhibit positive viscosity. The negative viscosity of the glycerol solution is attributed to the association of the solvent. The value of the ratio of absolute viscosity to molecular volume has been calculated for fifty non-associated organic liquids, and found to be approximately constant for members of the same class of compounds in the same series. From this ratio, it is inferred that the degree of association of glycerol exceeds that of water. The conclusion that the cation of the electrolyte and the association of the solvent determine negative viscosity is confirmed.

E. G.

Critical Opalescence. VICTOR ROTHMUND (*Zeitsch. physikal. Chem.*, 1908, 63, 54—82. Compare Abstr., 1898, ii, 503; also Friedländer, Abstr., 1901, ii, 643).—Mixtures of *n*-butyric acid and water, for a short interval above the critical solution temperature, exhibit a peculiar bluish opalescence or turbidity. This opalescence is very markedly diminished by dextrose, as well as by a number of salts, but is increased by naphthalene.

The temperature-coefficients of viscosity of these ternary mixtures about the critical solution temperature have been determined, and it is found that in this respect there is no essential difference between dextrose and the salts, on the one hand, and naphthalene, on the other. The influence of these substances on the critical opalescence must therefore be optical in its nature.

According to Donnan (*Chem. News*, 1904, 90, 139), the interfacial tension at temperatures slightly above the critical solution temperature is still positive for very small radii of curvature, but negative for all ordinary curvatures. If this is so, then the critical opalescence is due to the presence of very fine drops, and a mixture may be really non-homogeneous above the critical solution temperature. The author accepts this explanation, and suggests that the influence of a third substance in diminishing or increasing the opalescence observed in mixtures of *n*-butyric acid and water is due to an alteration of the refractive index of one of the phases. The nearer the refractive indices of the two phases the more difficult will it be to detect the opalescence, and any substance which brings the index of the one phase nearer to that of the other will apparently diminish the opalescence.

J. C. P.

Cause of the Decoloration of Coloured Liquids by means of Various Charcoals. FRITZ GLASSNER and WILHELM SCIDA (*Annalen*, 1908, 361, 353—362).—It was shown previously (Abstr., 1907, ii,

932) that lampblack, although free from nitrogen and ash, decolorises certain, especially basic, dyes. As this is not in agreement with the behaviour of charcoals in general, the authors have further studied the decolorising action of two specimens of lampblack and one of acetylene-black, all of which were free from nitrogen and ash, and were in a state of fine division.

When boiled with water, lampblack has an odour of camphor; the evaporation residue, as also that from the alcoholic extract, does not absorb dyes. The benzene extract, on the other hand, contains an oil, which has a terpene- or camphor-like odour, and is partly volatile with steam; the evaporation residue absorbs basic dyes from aqueous solutions. The lampblacks differ from animal charcoals in that absorbed dyes are readily dissolved by dilute acids, alkalis, or alcohol, although not by water. As it was observed that the amount of dye absorbed by a lampblack varies with its percentage of oxygen, experiments were performed with a large number of phenols, carboxylic acids, and sulphonic acids, and it was found that these have mostly a high absorptive power for basic dyes. Moreover, it is found that aurine, rosolic acid, and lamatoxylin form insoluble compounds with acid dyes. It is suggested that, whilst the absorptive power of animal charcoals results from the presence of substances containing the group $N \cdot C \cdot N$, that of the lampblacks depends on the presence of oxygen compounds, which form phenolic salts with basic, and oxonium salts with acid, dyes. The authors reply to criticisms by Rosenthaler (this vol., ii, 158). G. Y.

Diffusion of Albumin into Gelatin Jellies. G. MÖLLHAUSEN (*Zeitsch. Chem. Ind. Kolloide*, 1908, 2, 325).—When dry egg- or blood-albumin is placed on the top of a column of solidified gelatin solution containing 2–16% gelatin, the albumin forces its way into the jelly. After some days, a crack appears in the jelly, and this gradually increases in length. Rise of temperature favours the phenomenon. The albumin abstracts large quantities of water from the jelly during the diffusion process.

Addition of phenol to the albumin or jelly has no influence on the phenomenon. It also takes place when the albumin is dissolved previously in an equal weight of water, and when the jelly contains 10% of albumin. Diffusion of the mineral constituents and of the yellow colouring matter of the albumin into the jelly precedes the formation of the crack. The phenomenon cannot be ascribed to a tanning action. H. M. H.

Osmotic Pressure of Compressible Solutions of any Degree of Concentration. Part II. Cases in which both Solvent and Solute are Volatile. ALFRED W. PORTER (*Proc. Roy. Soc.*, 1908, 80, A, 457–465. *Compano Abstr.*, 1907, ii, 743).—The theory previously developed connecting osmotic pressure with vapour pressure in compressible solutions under any hydrostatic pressure is extended to the general case where the solute, as well as the solvent, has an appreciable vapour pressure. By means of a thermodynamic cycle, it is shown that the variation of vapour pressure of the solvent, and

also of the osmotic pressure, with variation of the hydrostatic pressure is expressed by the same equations as in the case where the solute is non-volatile. A simple proof is given that the vapour pressure of a pure liquid increases with hydrostatic pressure, by assuming that membranes can exist permeable to vapour, but not to liquid molecules. This proof cannot be extended to solutions, because a space variation of concentration would be set up by gravity under the conditions of the proof. The increased vapour pressure at a curved surface (Kelvin's formula), and also at an electrified surface, is supposed to originate in the higher hydrostatic pressure. R. J. C.

Osmotic Pressure of Sucrose Solutions at 10°. HARMON N. MORSE and H. V. MORSE (*Amer. Chem. J.*, 1908, 39, 667—680).—In view of the fact that the osmotic pressures of sucrose and dextrose solutions at 0° are somewhat in excess of the calculated gas pressures, whereas at 20° the two pressures are in agreement, it was considered desirable to determine the pressures of such solutions at several intermediate temperatures. The results of measurements of the osmotic pressure of sucrose solutions at 5° have already been recorded (*Abstr.*, 1907, ii, 744), and in the present paper an account is given of determinations made at 10°.

It is found that the osmotic pressure of sucrose solutions at 10°, like those at 0° and 5°, considerably exceeds the calculated gas pressure; it diminishes slightly from the 0.1*N* to the 0.4*N* solution, and then increases with increasing concentration. On comparing the pressures at 0° and 10°, some indications of a temperature-coefficient are observable, and this fact will be alluded to again when the results obtained at 15° are recorded. E. G.

Vapour Pressure and Osmotic Pressure of Strong Solutions. HUGH L. CALLENDAR (*Proc. Roy. Soc.*, 1908, 80, A, 466—500).—A theory of solutions is developed on the basis of a simple hypothesis connecting vapour pressure and concentration.

Arguments are first adduced to show how osmotic and other properties of solutions may be explained quantitatively as the result of differences in vapour pressure. An equation is obtained connecting vapour pressure with hydrostatic pressure, according to which a hydrostatic pressure of 2000 atmospheres is necessary to increase the vapour pressure of water four-fold at 27° if its compressibility remains constant.

Consideration of the hypothetical vapour sieve apparatus of Poynting (*Phil. Mag.*, 1881, [7], 12, 40) leads to the result that if a solution and the pure solvent, each contained in a vapour sieve tube, are in equilibrium with the same vapour column, they are in equilibrium with one another. The solution is necessarily under greater hydrostatic pressure than the pure solvent in this case. No disturbance will ensue if the solution sieve be actually surrounded by the solvent column, that is to say, the liquids are in osmotic equilibrium also.

A semi-permeable membrane may therefore be considered as a vapour sieve, and osmotic pressure may be defined as the hydrostatic pressure which must be applied to increase the vapour pressure of a solution to

that of the pure solvent. Conversely, liquids in osmotic equilibrium necessarily have the same vapour pressure.

The osmotic pressure of a solution is independent of hydrostatic pressure only if the solvent occupies the same volume in the solution as in the pure state. In a column of solution, the increase in vapour pressure downwards will be the difference between the increase due to hydrostatic pressure and the decrease due to the concentration of the solute by gravity, so that the gravity effect can be evaluated in the case of sucrose solutions from Berkeley and Hartley's vapour pressure measurements.

All the foregoing relationships can be simply established by equating to zero the work done in taking unit mass of solvent round a closed "osmotic circuit," and the author prefers this method to the isothermal cycle method employed by Porter (Abstr., 1907, ii, 713). An equation is obtained connecting hydrostatic pressure with latent heat of vaporisation, from which it appears that a pressure of 42 atmospheres would increase the latent heat of water by 1 cal.

The author's theory of solutions is based upon the hypothesis that the vapour pressure of a solution should be proportional to the ratio of the number of molecules of free solvent to the total number of molecules in the solution, molecular aggregates and hydrates being considered as single molecules. Thus if in a solution of n molecules of solute in N molecules of solvent each molecule of solute appropriates a molecules of solvent, the number of free molecules of solvent will be $(N - an)$, and the total number of molecules will be $(N - an + n)$. If p' and p'' be the vapour pressure of solvent and solution, $p'/p'' = (N - an)/(N - an + n)$. If sucrose be considered to hold 5 molecules of water of hydration, and if dextrose holds 2 molecules, this equation gives results which agree with Berkeley and Hartley's determinations of the osmotic pressure of these two substances within the limits of experimental error. The calculation must be made on a weight normal basis, and the hydration considered to be constant over the whole range of dilutions.

It is pointed out that the latent heat of fusion of ice has not the same value at temperatures below the freezing point as at 0° ; and that the "molecular lowering" of the freezing point of water by a dissolved substance, which depends on the latent heat of fusion of the solvent, must also vary with the temperature; furthermore, the freezing-point lowering is generally tacitly assumed to be directly proportional to the ratio of the difference of vapour pressures of ice and water to the vapour pressure of water. Therefore the author considers that the usual method of comparing the found with the calculated freezing-point depressions is futile in the case of strong solutions with a freezing point far removed from 0° .

Owing to the uncertainty of existing data for the vapour pressure of water below 0° , an exact formula connecting the vapour pressures of water and ice is not possible. A number of possible formulae are obtained by considering an "osmotic circuit," and the author finally adopts as the best approximation the simple expression $\log(p'/p) = -2.64t/273$, where p' and p are the vapour pressures of water and ice respectively at t° Centigrade. On this basis, the

freezing-point depressions of sucrose solutions agree very well with the calculated values when the hydration (α) is taken as 5. The depressions of methyl- and ethyl-alcohol solutions containing upwards of 20 mols. per 100 of solvent agree very well with the theoretical when the hydration is taken as 1. Glycerol appears to have hydration 2, but the freezing-point diagrams of acetone and formic acid lie very near the curve plotted with $\alpha = -1$, which suggests that the molecules of these substances associate with each other.

The application of the theory to electrolytes is complicated by questions of electrolytic dissociation. Assuming the number of free ions to be proportional to the conductivity, the following hydrate values are deduced from freezing-point data: $\text{HCl}, 5\text{H}_2\text{O}$; $\text{CaCl}_2, 9\text{H}_2\text{O}$; $\text{MgCl}_2, 12\text{H}_2\text{O}$; $\text{KCl}, \text{H}_2\text{O}$; $\text{NaCl}, 2\text{H}_2\text{O}$.

When the rise of the boiling point of solutions is considered from the author's point of view, sucrose appears to have the same hydration at 100° as at 0° (namely, $5\text{H}_2\text{O}$), except in the strongest solutions, where it is somewhat less. Potassium and sodium chlorides, on the other hand, are calculated to be more highly hydrated at 100° ($\text{KCl}, 4\text{H}_2\text{O}$; $\text{NaCl}, 6\text{H}_2\text{O}$) than at the freezing point.

On thermodynamic principles, the hydration of a substance cannot remain constant on diluting its solutions unless the heat of dilution is zero, as in the case of sucrose. Consideration of the special case of hydrochloric acid with its great heat of dilution indicates that the variation in hydration is not necessarily very great, particularly as the heat developed on dilution may be partly the result of increased dissociation.

The author claims to have made out a good *prima facie* case for a modified form of the hydrate theory of solutions, and compares his results with those obtained by other advocates of the same hypothesis.

R. J. C.

The Solubility Product. JULIUS STIEGLITZ (*J. Amer. Chem. Soc.*, 1908, 30, 946—954).—This paper contains a discussion of the principle of the solubility product which was enunciated by Nernst (Abstr., 1890, 3). From the data obtained by Arrhenius (Abstr., 1900, ii, 201) on the solubilities of silver acetate, propionate, butyrate, valerate, and chloroacetate in the presence of an excess of the corresponding sodium salt, the values of the solubility product ($C_{\text{Ag}} \times C_{\text{acid ion}}$) have been calculated. The results of Nernst's determinations (*loc. cit.*) of the solubility of silver acetate in presence of sodium acetate and silver nitrate respectively have also been re-calculated.

The results show that the solubility product has no theoretical foundation, and is only to be regarded as an approximate empirical principle. In the case of the organic silver salts, the principle is sufficiently in agreement with the observed facts to prove of some practical value, and this conclusion confirms the results obtained by other authors on the solubility of a salt in presence of other electrolytes having a common ion.

E. G.

Relationships between Chemical Composition, Crystalline Form, Hardness, and Density. I. VIKTOR PÖSCHL (*Zeitsch. phys. Chem.*, 1908, 59, 102—107).—The author has found certain

relationships between the crystalline form, hardness, and density of polymorphic minerals. Of two such polymorphic forms, that which has the greater density and the greater crystalline symmetry is never less hard than the second modification. If the modification of a lower degree of symmetry has the greater density, this form is never less hard than the second form.

The densities of a number of mineral sulphides have been compared with those of the constituent elements. In all cases, the density of the mineral is intermediate between the densities of the elements. The former can be approximately calculated from the latter by means of the simple mixture rule. The calculated densities are, in nearly all cases, somewhat smaller than the experimental values. The deviation between the two values is shown to be a periodic function of the atomic weight of the metal.

H. M. D.

Relation between the Crystalline Form and Chemical Constitution of the Picryl Derivatives. GEORGE JERUSALEM and WILLIAM J. POPE (*Proc. Roy. Soc.*, 1908, 80, A, 557—566).—The theory of Barlow and Pope as to the relation between crystalline form and chemical constitution (*Trans.*, 1906, 89, 1675; 1907, 91, 1150) has been further tested by application to a number of derivatives containing the 1:3:5-trinitrophenyl or picryl group.

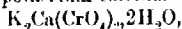
As regards crystalline structure, benzene and its simple derivatives belong to one of two types: one, derived from the closest-packed assemblage of equal spheres of hexagonal type, has the equivalence parameters $x:y:z=3.101:3.480:2.780$; the other is derived from the closest-packed assemblages of equal spheres of cubic type. The direction of z is perpendicular to the two planes containing the centres of the two sets of hydrogen atoms ordinarily numbered 1:3:5 and 2:4:6 respectively. Of the thirteen picryl compounds for which data are now available, it is shown that nine belong to the hexagonal type, and that for these compounds the effect of substitution is to alter two of the dimensions only, the third, of relative length 2.780, corresponding with the z dimension of benzene, remaining practically unaltered.

Among the substances belonging to the rhombohedral arrangement are *s*-trinitrobenzene and picric acid. On passing from *s*-trinitrobenzene to the similarly-constituted tribromodinitrotoluene there is practically no change in the equivalence parameters, corresponding with the fact that the valencies of the groups displaced are the same as those of the original groups.

G. S.

Dimorphism of Potassium Calcium Chromate. A. V. RAKOWSKI (*Bull. Acad. Sci. St. Petersburg*, 1908, 10, 905—917).—The object of the research was to test the question whether two polymorphic forms of a substance can belong to the same crystalline system.

The β - and α -forms of potassium calcium chromate,



the crystalline characters of which are discussed in detail, are prepared by the action of unslaked lime on potassium dichromate, the quantity of each modification formed depending on the pressure and

temperature at which crystallisation occurs, and on the presence of other substances in the solution.

The α -modification belongs to the rhombic system [$a:b:c=2.3629:1:2.0946$], $D_{15}^{25} 2.449$ (2.413 for large crystals), molecular heat of solution 6993 Cal. The β -modification belongs to the hemihedral triclinic system [$a:b:c=0.7591:1:0.8915$; $\alpha=86^{\circ}10'$; $\beta=94^{\circ}4'$; $\gamma=81^{\circ}40'$], $D_{15}^{25} 2.611$ (2.600 for large crystals), molecular heat of solution 5458.8. Solubility curves and tables are given for both varieties, showing that the solubility of each increases with the temperature, and that the α -modification is unstable with reference to the β -form, the transition-temperature of the former being at about 0° .

At 97° the dry salt decomposes, thus: $K_2Ca(CrO_4)_2 \cdot 2H_2O \rightleftharpoons K_2CrO_4 + CaCrO_4 + 2H_2O$. A solution saturated at 20° becomes cloudy at $55-60^{\circ}$, and the precipitate formed at $90-100^{\circ}$ corresponds with the formula $K_2CrO_4 \cdot 4CaCrO_4 \cdot 2\frac{1}{2}H_2O$; at 260° the water in this salt commences to separate.

Z. K.

Liquid Crystals. TH. ROTARSKI (*Ber.*, 1908, 41, 1994—1998). Clear Transparent Crystalline Liquids. DANIEL VORLÄNDER (*ibid.*, 2033—2052).—See this vol., i, 640, 641.

Theory of Colloids. EDUARD JORDIS (*Zeitsch. Chem. Ind. Kolloide*, 1908, 2, 361—367).—A critical examination of the principles underlying a theory of colloids. In this first portion of the paper, the various possible types of homogeneous mixtures which may be classified under the head of solutions are discussed. A hydrosol regarded as a homogeneous mixture of solid and liquid particles is considered to satisfy the requirements of the definition of a solution.

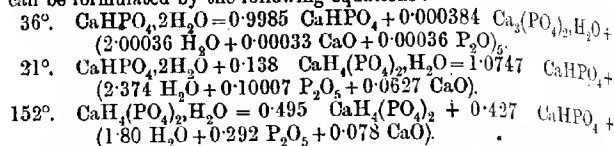
H. M. D.

Diagrammatic Representation of Equilibria between Acids and Bases in Solution. LAWRENCE J. HENDERSON (*J. Amer. Chem. Soc.*, 1908, 30, 954—960).—Diagrams have been constructed which express the requirements of the concentration law regarding the equilibrium in solution between strong acids and bases, and between strong bases and acids, of all strengths, but are not suitable for solutions of high acidity or alkalinity. These diagrams accurately define the conditions of equilibrium at all concentrations of hydrogen and hydroxyl ions, between all acids and bases, with the exceptions already mentioned, and in all mixtures of such substances. They also define all isohydric solutions of such substances in which this quality depends only on the equality of the concentration of hydrogen and hydroxyl ions.

E. G.

Calcium Phosphates. III. The System $CaO-P_2O_5-H_2O$. HENRY BASSETT, JUN. (*Zeitsch. anorg. Chem.*, 1908, 59, 1—55. *Compt. rend. Proc.*, 1906, 315).—By means of dilatometer experiments, the position of quintuple points on the space model of the three-component system $CaO-P_2O_5-H_2O$ has been determined. At these temperatures

changes take place which, on the basis of solubility measurements, can be formulated by the following equations:



The formulæ in brackets represent the composition of the solutions in equilibrium with the solid phases at the various quintuple points.

As the result of measurements of solubility at 25°, 40°, and 50°, isothermals have been obtained, on the basis of which the space model for the three-component system has been constructed.

The observation of van't Hoff, that the velocity with which changes in complicated systems take place diminishes with increasing basicity of the acid radielo and increasing valency of the metal, is confirmed by the author's observations.

The paper concludes with certain speculations as to the nature of the calcium phosphates which have been examined, and as to the condition of the phosphoric acid contained in soils. H. M. D.

The Ternary System: Mercuric Chloride, Ammonium Chloride, and Water at 30°. P. A. MEERBURG (*Zeitsch. anorg. Chem.*, 1908, 59, 136—142; *Chem. Weekblad*, 1908, 5, 429—433).—The three-component system has been examined according to the methods of the phase rule. Data are recorded representing the composition of the aqueous solutions in equilibrium with the various combinations of solid phases. Of the various double salts described in the literature, namely, $\text{HgCl}_2 \cdot \text{NH}_4\text{Cl}$; $\text{HgCl}_2 \cdot \text{NH}_4\text{Cl} \cdot \text{H}_2\text{O}$;

$\text{HgCl}_2 \cdot 2\text{NH}_4\text{Cl} \cdot \text{H}_2\text{O}$;
 $9\text{HgCl}_2 \cdot 2\text{NH}_4\text{Cl}$, and $3\text{HgCl}_2 \cdot 2\text{NH}_4\text{Cl} \cdot 4\text{H}_2\text{O}$, the first and last do not exist at 30° according to the author's experiments. These, however, indicate the existence of a double salt of the composition
 $3\text{HgCl}_2 \cdot 2\text{NH}_4\text{Cl} \cdot \text{H}_2\text{O}$.

Of the various double chlorides, $\text{HgCl}_2 \cdot 2\text{NH}_4\text{Cl} \cdot \text{H}_2\text{O}$ is the only one which can be recrystallised from its aqueous solution. H. M. D.

Calculation of Hydrocarbon Equilibria. H. VON WARTENBERG (*Zeitsch. physikal. Chem.*, 1908, 63, 269—272).—An error having crept into the calculation of the methano equilibrium in the earlier paper (this vol., ii, 26), this calculation is revised, with the result that the deviation between observed and calculated figures is greater than before. No complete explanation of the discrepancy can be expected until the equilibrium has been subjected to further experimental investigation. J. C. P.

Statics and Kinetics of the Transition which occurs in Liquid Sulphur. Heat of Fusion of Monoclinic Sulphur. ALBERT WIGAND (*Zeitsch. physikal. Chem.*, 1908, 63, 273—306).—The heat of fusion of monoclinic sulphur has been determined by an electrical method. A weighed quantity of sulphur was put in a glass

vessel inside an oil calorimeter, which in its turn was surrounded by an electric bath kept at 116° . When it was certain that the sulphur had been completely converted into the monoclinic variety, a known amount of energy was added by passing a current through a wire embedded in the sulphur; the added heat was so adjusted as to melt all the sulphur and to raise the temperature of the calorimeter about 5° more or less. The value so found for the heat of fusion is 10.4 cal. for 1 gram of sulphur, with a possible error of $\pm 3\%$.

From this figure, the molecular depression constant for monoclinic sulphur is calculated by van't Hoff's formula; if further 42.5° is taken as the depression due to a gram atom of the insoluble variety (see Smith, Abstr., 1903, ii, 139) the number of atoms in a molecule of this insoluble sulphur works out to 6.9. The author, however, considers that 8 is more probably the correct number (see Smith, *loc. cit.*), and S_8 is accordingly taken as representing the molecular condition of both the soluble and the insoluble modifications.

The view that the two molecules have the same number of atoms, and that liquid sulphur is subject to a reversible isomeric change, $S_{8\text{sol.}} \rightleftharpoons S_{8\text{insol.}}$ is supported by Schaum's figures, which show how the freezing point of a sample of sulphur falls when it is kept for gradually increasing periods at temperatures above 120° . From these figures, it is possible to calculate satisfactory velocity-coefficients for the foregoing isomeric change, and from the values of the coefficient at different temperatures it is calculated that the heat absorbed when 1 gram of liquid soluble sulphur is transformed into the liquid insoluble modification is 21.1 cal.

From all this, it appears that the transition which occurs in liquid sulphur is an intramolecular rearrangement, which does not involve any change in the molecular weight (compare Smith, *loc. cit.*). J. C. P.

Affinity Constants of Organic Acids determined with the Help of Indicators. EDUARD SALM (*Zeitsch. physikal. Chem.*, 1908, 63, 33—108).—The affinity constants of sixty-eight organic acids have been determined by the indicator method already described (Friedenthal, Abstr., 1904, ii, 288; Salm, Abstr., 1904, ii, 536; 1906, ii, 218. Compare also Velej, Trans., 1907, 153, 1246). Solutions of hydrochloric acid were used as standards of comparison, and the indicators employed were dimethylaminoazobenzene, methyl-orange, and tropæolin-10. In the great majority of cases, the affinity constants deduced in this way are in good agreement with the values reached by the conductivity method. In the case of formic and oxalic acids, the value of the expression $\alpha^2/(1-\alpha)V$ falls off on dilution. J. C. P.

Saponification of Glycerides during Ester Exchanges in Homogeneous System. MILAN J. STRITAR and RICHARD FANTO (*J. pr. Chem.*, 1908, [ii], 78, 35—41. Compare Abstr., 1904, i, 843; 1907, i, 277).—The authors have calculated the results of their experiments on the saponification of rape-seed oil, as suggested by Wegscheider (this vol., ii, 165). If it is assumed that at the moment when the saponification is stopped the product is a mixture of diglyceride and ester, the mean partition coefficient for the second

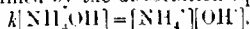
minute of the experiment is found to be 1.88, whilst that for the third minute is 1.02, hence in the second minute about twice as much glyceride as ester is saponified, whereas in the third minute the amounts are approximately equal. If, on the other hand, it is assumed that, at the moment of stoppage of the saponification, the combined glycerol is present as a mixture of tri- and mono-glycerides, the partition coefficient for the second minute is 2.35, and for the third minute, 1.28. Here, again, the saponification of the glyceride decreases in comparison with that of the ester. These results are in agreement with the authors' views as to the mechanism of the saponification of fats.

The remainder of the paper is a reply to Kremann (this vol., i, 129).
G. Y.

Schütz's Rule for Reaction Velocities. SVANTE ARRHENIUS (*Meddel. K. Vetensk. Nobelinst.*, 1908, 1, No. 9, 1—17).—The author discusses a relationship pointed out by Schütz (Abstr., 1885, 1147) in connexion with the rate of action of pepsin on albumin. According to this, the quantity of albumin transformed in a given time by different amounts of pepsin is proportional to the square root of the pepsin concentration, provided that the reaction is not allowed to proceed too long. The same relationship has since been found in the action of trypsin and of lipolytic ferments.

It is shown that for the validity of Schütz's rule, the reaction velocity must be inversely proportional to the quantity of substance already transformed. This condition is fulfilled when one of the reacting substances is influenced by one of the products of reaction in such a way that the active mass of the former is inversely proportional to the active mass of the latter.

An example of such a reaction is afforded by the saponification of an ester present in large excess by a weak base, like ammonia. The reacting component to be considered is the OH' ion, and the active mass of this is determined by the dissociation equation



As saponification proceeds, the concentration of the NH_4^+ ions increases proportionally with the amount of ester saponified, and corresponding with the dissociation equation the concentration of the OH' ions diminishes in inverse proportion.

Measurement of the rate of saponification of ethyl acetate by ammonia, under the conditions specified, has shown that Schütz's rule is valid until about half the ammonia has been transformed. From this point, the deviations between experiment and the requirements of the rule increase very rapidly. The progress of the reaction was followed by determination of the electrical conductivity of the solution.

An action similar to that of an ammonium salt on ammonia is supposed to determine the similar progress of the action of pepsin on albumin. The cause of the action is supposed to be the combination of the reaction product with the ferment.
H. M. D.

Review of the Various Theories of Passivity. Fresh Observations on the Passivity of Iron, Nickel, and Chromium. CARL FREDENHAGEN (*Zeitsch. physikal. Chem.*, 1908, 83, 1-47. Compare Abstr., 1903, ii, 353; 1906, ii, 76; also Finkelstein, Abstr., 1902, ii, 81; Müller, Abstr., 1904, ii, 610).—The passivity of metals is supposed by some to be due to the formation of a film of oxide on the surface of the metal, and by others to be due to the change of the metal into another modification. The author rejects both these explanations, and argues in favour of the view, previously upheld by him (*loc. cit.*), that in the passive condition the metal is protected by a surface layer of gas.

The experiments recorded in the paper consisted in applying a gradually increasing or a gradually diminishing *E.M.F.* to an iron, nickel, or chromium electrode immersed in sulphuric acid, and determining (1) the *P.D.* at this electrode, and (2) the strength of the polarisation current. The *P.D.* of the metal electrode at the point where passivity or activity sets in is not well defined, and this supports the view that the passivity phenomena do not depend on the formation either of an oxide film or of another modification of the metal, but that they are ultimately related to the rate at which the metal becomes charged with oxygen. Further, the *P.D.* recorded when passivity or activity sets in is markedly affected by slight changes in the strength of the sulphuric acid, and rise of temperature has a notable influence in favouring the active condition. At an iron electrode immersed in sulphuric acid and subjected to anodic polarisation, some reactions take place which lead to the production of oxygen, and others use up oxygen. According to the author, the passive condition is reached when the oxygen polarisation extends uniformly over the whole surface of the electrode, and the reappearance of the active state on lowering the polarisation *E.M.F.* is due to the fact that the reactions which use up oxygen begin to overbalance those which produce oxygen.

J. C. P.

The Excitation and Regulation of Catalytic Pulsations by means of an Electric Current. GEORG BREDIG and ERNST WILKE (*Biochem. Zeitsch.*, 1908, 11, 67-81).—Bredig and Weinmayer have shown that the catalytic decomposition of hydrogen peroxide into water and oxygen, a reaction discovered by Thénard, takes place under certain conditions in rhythmical periods. The influence of electrical currents on this rhythm has been studied. The peroxide solution was placed in a vessel, with mercury at the bottom, into which an electrode passed. The other electrode was placed in the peroxide solution. The apparatus was so arranged that the evolution of oxygen could be graphically recorded. It was found that by means of a constant current, alternating current, or induction shock, an a-periodic chemical change could be converted into a period change. Also, that a spontaneous rhythmical catalysis could be modified as regards its pulsation form, its period, or intensity by means either of a constant or alternating current. The relations of these phenomena to certain biological processes, such as nerve stimulation, are discussed. S. B. S.

Catalysis in Heterogeneous Systems. Decomposition of Chromous Chloride by means of Platinum. CASIMIR JACZYŃSKI (*Bull. Acad. Sci. Cracow*, 1908, 398—401).—The decomposition of chromous chloride between platinised platinum plates has been examined. Between 25° and 55° the reaction appears to be unimolecular. When smooth platinum foil is used, the velocity is some three times smaller than with platinised plates. The velocity of decomposition varies with the rate at which the liquid is stirred. The temperature-coefficient, 2.75% per 1°, is the same as for ordinary diffusion experiments, so that the velocity appears to depend entirely on diffusion, and the actual chemical reaction proceeds with enormous velocity. The effect of non-electrolytes, for example, alcohol and sugar, on the velocity is exactly the same as for other diffusion experiments.

The velocity depends on the amount of hydrochloric acid present, and is accelerated by the addition of potassium or calcium chloride, but diminished by the addition of chromic chloride. The reaction does not proceed in the presence of potassium chloride unless free acid is also present.

These phenomena are accounted for by the assumption of the formation of an additive compound of chromous and chromic chlorides, which has a slower rate of diffusion. Addition of hydrochloric acid, potassium chloride, or calcium chloride tends to decompose this compound, liberating chromous chloride, whereas increase in the concentration of the chromous chloride, or addition of chromic chloride, increases the amount of the additive compound.

Iodine and mercuric chloride do not affect the decomposition, whereas small amounts of hydrogen sulphide diminish the rate of decomposition; hydrocyanic acid acts less readily. J. J. S.

Catalysis. VI. Catalysis of Imino-esters. HERMANN I. SCHLESINGER (*Amer. Chem. J.*, 1908, 39, 719—771. Compare Stieglitz, this vol., ii, 167, 168; Derby, this vol., i, 419).—Measurements have been made of the velocity of hydrolysis of the hydrochlorides of methyl and ethyl iminobenzoates in 1.10 and 1.40 molar solutions, and also of the velocity of decomposition of methyl, ethyl, and *n*- and *iso*-propyl iminobenzoates, and of methyl *m*-nitroiminobenzoate, under the influence of varying proportions of barium hydroxide. A study has also been made of the decomposition of methyl iminobenzoate in aqueous solutions. The results are tabulated, and lead to the conclusions which have already been expressed by Stieglitz (*loc. cit.*). E. G.

Potential Energy of the Elements. DANIEL J. RANKIN (*Chem. News*, 1908, 97, 302—303).—An element is regarded as a system of energy which under normal conditions exist in two states, static or intrinsic energy and potential energy. The intrinsic energy is incapable of being freed, is inert, and is uninfluenced by any ordinary extraneous energy whatsoever. The potential or free existing energy permits of calculation in terms of thermal calories, and this the author has done for seventy-seven elements. In thermochemical measure

ments, the "heat of formation" is the value of that portion of the potential which is lost or integrated, and the resulting compound undergoes diminution or increase in volume in a fixed ratio to the loss or gain of potential. For most elements the atomic weights of which are below 60, it has been found that the ratio of loss of potential to loss of volume = 1:1, except in the zinc, cadmium, mercury family, where it is 1:0.76, and with sodium, calcium, and potassium, 1:0.65 nearly. Examples are given showing that it thus becomes possible to calculate the density of a substance, such as solid oxygen or chlorine, when existing in a chemical compound; also, the specific gravity of a chemical compound when the heat of formation is given.

J. V. E.

Deduction of Stoichiometric Laws. F. WALD (*Zeitsch. physikal. Chem.*, 1908, 63, 307—324).—In replying to de Vries (this vol., ii, 366), the author maintains and extends his earlier views as to the possibility of deducing all quantitative chemical relationships from purely qualitative data. The limitations of the atomic hypothesis and of the theory of valency are emphasised. The author shows that of all the facts to which the name "stoichiometric" can be applied, the most general is this, that a qualitative analysis is possible without a quantitative.

J. C. P.

Safety Apparatus for Ovens, Baths, &c. LOUIS L. DE KONINCK (*Bull. Soc. chim. Belg.*, 1908, 22, 192—195).—A modified form of H. Michaelis' apparatus (*Abstr.*, 1897, ii, 169) devised to automatically cut off the supply of gas to burners placed under baths, &c., provided with constant supply arrangements for water, in case the water supply is temporarily stopped, is described and figured.

T. A. H.

Simple Arrangement for Continuous Extraction with a Solvent of Inconstant Boiling Point. EMIL WÖRNER (*Chem. Zeit.*, 1908, 32, 608).—When using a Zuntz pattern Soxhlet apparatus for extracting with a solvent of no very definite boiling point, such as light petroleum, a mixture of alcohol and chloroform, &c., it is recommended that a wire spiral be placed round the extraction cup instead of the fragile glass tube. In this manner, the solvent of slightly lower boiling point is prevented from accumulating in the upper region of the tube, and by having intermediate porous layers of sand or wadding the extraction takes place quite rapidly.

J. V. E.

Circulation Stirrer for Liquids. ROBERT GOETZE (*Chem. Zentr.*, 1908, i, 1509—1510; from *Zeitsch. Chem. Apparatenkunde*, 1908, 3, 147).—A tubular glass stirrer having four short, horizontal open limbs is made to revolve rapidly in a flask-shaped vessel containing the liquid, so that the liquid is forced by the revolving limbs up a side-tube situated exactly opposite them, the action being similar to that of a centrifugal pump. The return liquid enters the vessel through the hollow spindle of the stirrer.

J. V. E.

Inorganic Chemistry.

Decomposition of Water Vapour by Electric Sparks. ALFRED HOLT, jun., and EDWIN HOPKINSON (*Phil. Mag.*, 1908, [vi], 16, 92—110).—The authors have examined the decomposition of water vapour and carbon dioxide by electric sparks, and the conclusion is drawn that the separation and distribution of the decomposition products noted by previous observers in the case of water vapour is not an electrical phenomenon, but is the result of gaseous diffusion. The decomposition effects cannot be explained by ordinary electrolysis.

When sparks are passed through water vapour contained in an apparatus of the type used by Chapman and Lidbury (*Trans.*, 1902, 81, 1301), hydrogen and oxygen are produced in the path of the spark. On account of its greater rate of diffusion, the hydrogen tends to become uniformly distributed throughout the apparatus, even when a rapid current of vapour is passing through it. The distribution of the oxygen depends on the relative position of the tube, through which the water vapour enters the sparking vessel, in reference to the anode and cathode. When the water vapour enters at the anode, the greater portion of the oxygen will be swept out at the cathode and vice versa. With the entrance tube near the centre of the spark-gap, equal quantities of oxygen are swept towards the separate poles. This view is supported by experimental data, and it is shown that, under like conditions, the products of decomposition of carbon dioxide, corresponding with their nearly equal rates of diffusion, are always distributed symmetrically.

The observation made by Chapman and Lidbury (*loc. cit.*) that the total quantity of water vapour decomposed, and the extent of the separation of the hydrogen and oxygen, is much greater when the current of water vapour enters the discharge tube in the neighbourhood of the cathode instead of near the anode is confirmed. To explain this, it is supposed that the metallic spray produced by the disintegration of the cathode exerts a catalytic action, which results in a greatly increased union of the products of dissociation. With aluminium electrodes, which do not yield such a metallic spray, the effect is not observed. Using platinum electrodes, the effect diminishes when thicker wires are used, corresponding with diminished disintegration; it is also smaller when the bulbs surrounding the electrodes are made larger.

The behaviour of other metallic electrodes has also been examined. Metals which oxidise when heated in air behave like aluminium; those which do not oxidise or which form a volatile oxide, as in the case of osmium, behave like platinum. Silver and palladium are exceptions. Although silver sprays readily, it does not appear to have any effect on the union of the dissociation products. The behaviour of platinum is traced to its exceptionally high catalytic activity.

On this view, J. J. Thomson's observation, that the pole at which the excess of hydrogen or oxygen appeared in his experiments depended on the length of the spark, can also be explained.

H. M. D

Activity of the Halogens, Chlorine, Bromine, and Iodine in Relation to the Metals in General. M. C. SCHUYTEN (*Chem. Zeit.*, 1908, 32, 619—620. Compare this vol., ii, 31).—The chlorides of twenty-four metals have been digested with bromine and with iodine, and the bromides of twenty-three metals digested with iodine. After testing the residues from the metallic chlorides and showing the absence of free halogen, they were treated with chlorine water and again tested, when it was generally found that some bromine or iodine was liberated. In the case of the bromides digested with iodine, the dry test for iodine generally indicated the presence of small quantities of that halogen. Whether addition or substitution of halogen takes place under these conditions, the author is at present unable to decide.

J. V. E.

Variation of the Surface Tension of Sulphur with Rise of Temperature: SA^1 and SA^2 . GEORGES CAPELLE (*Bull. Soc. chim.*, 1908, [iv], 3, 764—767).—Smith has shown (Abstr., 1905, ii, 382, 580) that between the melting point (125°) and 160° a definite liquid form of sulphur (SA) exists, and that at 160° this passes into a new form (S_μ). The author confirms and extends this view from observations on the anomalous change in the surface tension of sulphur as the temperature is raised from 125° to 160° . Between 125° and 142° a slight increase in surface tension takes place, and between 142° and 160° a large and rapid increase. At 160° the liquid becomes viscous, and observations cannot be carried further. It is suggested that Smith's SA is divisible into two species, one (SA^1) existing between 125° and 142° , and the other (SA^2) between 142° and 160° , but SA^2 may be merely a mixture of SA^1 with S_μ , the formation of the latter commencing at 142° and becoming complete at 160° .

T. A. H.

Colloidal Sulphur. M. RAFFO (*Zeitsch. Chem. Ind. Kolloide*, 1908, 2, 358—360).—Soluble colloidal sulphur is obtained when a concentrated solution of sodium thiosulphate is added very slowly to cooled concentrated sulphuric acid (D 1.84). If the addition of the thiosulphate solution is effected too rapidly, a large proportion of insoluble sulphur is formed. The changes taking place are represented by the equations: (1) $H_2S_2O_3 = SO_2 + H_2O + S$ (insoluble); (2) $H_2S_2O_3 = H_2S + SO_3$; $2H_2S + SO_3 = 2H_2O + 3S$ (soluble).

In order to separate the soluble and insoluble sulphur, the thick, cloudy liquid is diluted somewhat, heated to 80° , and filtered through glass-wool. It is then left in a cool place for twelve hours, again heated and filtered, and these operations are repeated until the whole of the insoluble sulphur has been removed. The end product is a cloudy, yellowish-white mass, which, on warming, yields a perfectly clear yellow liquid. On cooling, the colloidal sulphur separates, and is removed by centrifuging, washed with a little cold water, again centrifuged, and dissolved in the least possible quantity of water. The liquid is neutralised by addition of sodium carbonate, which causes the sulphur to separate, and, after centrifuging, a residue of very nearly pure soluble sulphur is obtained.

On removing the sodium sulphate from the neutralised solution by

dialysis, it is found that the solution became unstable and insoluble sulphur separates. The conclusion is drawn that a pure aqueous solution of colloidal sulphur cannot be obtained. Separation also takes place on addition of various electrolytes. The sulphur precipitated by sodium chloride or nitrate dissolves on warming or on dilution, and that precipitated by potassium chloride, nitrate, or sulphate is insoluble. Precipitation does not take place, in general, on the addition of ammonium sulphate, nitrate, or chloride, or of sodium sulphate. Dilute unneutralised solutions remain clear for long periods, although small quantities of rhombic and monoclinic sulphur are gradually deposited. Concentrated solutions become cloudy in consequence of the separation of insoluble sulphur.

H. M. D.

Spontaneous Oxidation of Sulphur and Sulphides. Egidio POLLACCI (*Boll. chim. farm.*, 1908, 47, 363—368).—Moist sulphur in a state of fine division oxidises in the air to sulphuric acid, the action being accelerated by light. In absence of oxygen, sulphur does not decompose water. Pure oxygen or hydrogen peroxide does not bring about the oxidation, and the active agent present in the air is considered to be ozone.

Metallic sulphides also oxidise in a moist state, the first products being the oxide and sulphur, the latter then oxidising to sulphuric acid. Solutions of hydrogen sulphide do not oxidise directly to sulphuric acid, the first process being the production of water and sulphur, followed by oxidation of the latter. The sulphides of iron, manganese, cobalt, gold, silver, platinum, antimony, and titanium oxidise rapidly, those of calcium, barium, strontium, potassium, arsenic, cadmium, mercury, and tin less rapidly, and those of zinc and copper very slowly.

C. H. D.

Preparation of Sulphur Trioxide. RUDOLF FRANK (D.R.P. 194879).—One of the chief difficulties of the contact process for sulphuric acid is the sensitiveness of the contact material to impurities in the sulphur dioxide, and another is the maintenance of a definite temperature during the operation in order to avoid a reverse chemical change. These difficulties are overcome by compressing sulphur dioxide and oxygen under a pressure of 100 atmospheres, when a complete condensation to sulphur trioxide occurs. By rapidly releasing the pressure, the trioxide may be obtained in a solid condition without appreciable loss of vapour.

G. T. M.

Preparation of Sulphuric Acid. OSKAR BENDER (D.R.P. 195810).—A mixture of oxygen and sulphur dioxide is introduced into a generator furnace in which water-gas is being produced and then burnt. The heat generated induces the combination of these gases to form sulphur trioxide, and the water produced serves to hydrate this substance, forming sulphuric acid. When air is employed, a certain amount of nitric acid is also produced, which exerts its catalytic action on the mixture of gases and increases the formation

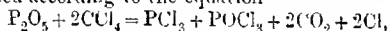
of sulphuric acid. The furnace is fed with sulphur or sulphur-containing materials.

G. T. M.

Quantitative Vaporisation of Phosphoric Acid from Phosphates in a Current of Chlorine and Carbon Tetrachloride or of Carbon Tetrachloride Only. PAUL JANNASCH and W. JULKE (*J. pr. Chem.*, 1908, [ii], 78, 21—28. Compare Abstr., 1907, ii, 864).—It is now found that phosphoric acid can be distilled quantitatively from calcium, sodium, or potassium phosphate if the phosphate is thoroughly ground with quartz powder and the mixture heated in a current of chlorine which has been passed through carbon tetrachloride. The calcium phosphate was heated for four hours at a dark red, and for two hours at a bright red, heat in a quartz boat, and the sodium and potassium phosphates for nine hours at a bright red heat in a gas-carbon boat, in a glass tube. The phosphoric acid distils the more quickly the slower the current of chlorine and carbon tetrachloride.

Phosphoric acid does not distil, even in traces, when magnesium phosphate is heated alone or in admixture with wood charcoal in a current of dry ammonia at a bright red heat (compare Heraeus, Abstr., 1903, ii, 82). Ammonium phosphate, on the other hand, volatilises partly in a current of ammonia, but does not attack the glass tube as when distilled in a current of carbon dioxide; the ammonium phosphate leaves a residue of vitreous phosphoric acid, which is almost insoluble in water or mineral acids.

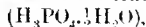
When heated in a current of carbon tetrachloride at a moderate red heat, ferric phosphate is completely volatilised; if the cool end of the tube is packed loosely with glass-wool, ferric chlorido is here deposited quantitatively, whilst the mixture of phosphorus trichloride and oxychloride, formed according to the equation



is readily driven over into the receiver.

G. Y.

Hydrates of the Phosphoric Acids. HENRI GIRAN (*Compt. rend.*, 1908, 146, 1270—1272).—The freezing-point curve of aqueous solutions of orthophosphoric acid shows two minima and a single maximum. The minima characterise two eutectics of the composition $(\text{H}_3\text{PO}_4, 0.135\text{H}_2\text{O})$, m. p. 22.5° , and $(\text{H}_3\text{PO}_4, 3.205\text{H}_2\text{O})$, m. p. -81° . The maximum at 29° indicates the existence of the hydrate



for which Joly found m. p. 27° (compare Abstr., 1885, 482). The freezing-point curve for pyrophosphoric acid is similar in form. The two eutectics correspond with the formulæ $(\text{H}_4\text{P}_2\text{O}_7, 1.25\text{H}_2\text{O})$, m. p. 23° , and $(\text{H}_4\text{P}_2\text{O}_7, 6.87\text{H}_2\text{O})$, m. p. -75° . The maximum characterises the hydrate $(\text{H}_4\text{P}_2\text{O}_7, 1.5\text{H}_2\text{O})$, m. p. 26° . This compound has been isolated as unstable needles, readily undergoing conversion into orthophosphoric acid. Measurement of its heat of dissolution proves it to be less stable than the hydrate of orthophosphoric acid.

Only a small portion of the curve for metaphosphoric acid can be studied, since solutions containing less than 63% of water are converted on cooling into a vitreous mass, which refuses to crystallise.

W. O. W.

Molecular Weights of the Phosphoric Acids determined by Cryoscopy. HENRI GIRAN (*Compt. rend.*, 1908, 146, 1303—1306).—The molecular weights of metaphosphoric and pyrophosphoric acids in acetic acid solution diminish after a lapse of time, and finally reach a limit depending on the concentration of the solution. From extrapolation in the curve representing variation of molecular weight with age of solution, it is found that at the moment of solution, metaphosphoric acid has a molecular weight corresponding with the formula $5(\text{HPO}_3)_2$, whilst pyrophosphoric acid has the formula $3(\text{H}_4\text{P}_2\text{O}_7)$. The molecular weight of orthophosphoric acid varies only slightly with time; the values obtained varied from 111.9 to 127.1, according to the concentration of the solution. The acid should probably be represented by the formula $(\text{H}_3\text{PO}_4)_3$. Orthophosphoric and pyrophosphoric acids have the same molecular weights in the liquid as in the solid form.

W. O. W.

The Removal of Arsenic from Liquids and Gases. CHEMISCHES FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 194864).—In order to free a liquid, such as concentrated sulphuric acid, from arsenic, it is treated with strong hydrochloric or hydrofluoric acid, and then mixed intimately with benzene. On drawing off the latter liquid, it is found to contain all the arsenic as chloride or fluoride, and, when freed from this impurity by treatment with water, it may be employed in removing arsenic from further quantities of sulphuric acid. Dichlorobenzene may also be employed for this purpose, and, owing to its higher boiling point, is preferably used in the removal of arsenic from gases by allowing it to flow down towers through which the gaseous mixtures are passing.

G. T. M.

Ammoniacal Arsenic Trichloride. ADOLPHE BESSON and GEORGES ROSSET (*Compt. rend.*, 1908, 146, 1266—1267. Compare Abstr., 1899, 1052; Hugot, Abstr., 1904, ii, 559).—When dry, gaseous ammonia acts on arsenic trichloride at -20° , a bright yellow solid, $\text{AsCl}_3 \cdot 4\text{NH}_3$, is formed; this sublimes completely when heated in a vacuum at 200° , forming a yellow, horn-like substance, $2\text{AsCl}_3 \cdot 7\text{NH}_3$. When the former compound is treated with liquid ammonia, it loses its colour, and remains colourless when the excess of ammonia is driven off. When extracted with liquid ammonia, ammonium chloride is removed and a white, insoluble residue obtained, the composition of which agrees with that of the imide, $\text{As}_2(\text{NH})_{12}$. On making an intimate mixture of the portions soluble and insoluble in liquid ammonia, a substance is obtained which differs from the original compound in that it is not completely volatile at 200° , and when treated with sulphuric acid yields only a small quantity of arsenic trichloride.

These experiments lead to the conclusion that liquid ammonia acts on the compound $\text{AsCl}_3 \cdot 4\text{NH}_3$ as a reagent, and not merely as a solvent. Arsenic trichloride also reacts with $\text{AsCl}_3 \cdot 4\text{NH}_3$, giving rise to ammonium chloride and a substance or mixture of substances, the composition of which is indicated approximately by the formula $\text{As}_3\text{Cl}_5\text{N}_2\text{H}_4$. The identity of this product has not been established.

W. O. W.

Tellurides of Arsenic and Bismuth. Cryoscopic Constant of Tellurium. HENRI PÉLABON (*Compt. rend.*, 1908, 146, 1397—1400).

—Arsenic dissolves readily in molten tellurium. Examination of the freezing-point curve of the solution indicates the existence of the compound As_2Te_3 , characterised by a maximum at 362° . This telluride crystallises in long, silver-white needles having a pale yellow tint. The freezing-point curve for solutions of bismuth in tellurium has been completely followed. A maximum occurs at 583° , corresponding with the compound Bi_2Te_3 . The freezing points of solutions of these two tellurides in excess of tellurium have been determined, and the cryoscopic constant of tellurium calculated. The value $K=517$ was obtained from As_2Te_3 , whilst the bismuth compound gave $K=528$. These numbers agree closely with those already determined for this constant.

By applying Robertson's formula (*Trans.*, 1903, 81, 1233), the latent heat of fusion of tellurium is found to be 20—21 Cal.

W. O. W.

Synthesis of Boron Sulphide from Ferroboron and Manganoboron. JOSEF HOFFMANN (*Zeitsch. anorg. Chem.*, 1908, 59, 127—135. Compare *Abstr.*, 1907, ii, 82).—The formation of boron sulphide by passing a current of dry hydrogen sulphide over ferroboron and manganoboron at the melting point of antimony has been examined in detail. The ferroboron is more rapidly decomposed than the manganoboron, and a better yield is obtained with the former material. In both cases, only a portion of the contained boron can be converted into the sulphide.

Boron sulphide loses weight on exposure to the air, and hydrogen sulphide is evolved. It also changes when kept in the dark in closed vessels. Water, alcohol, and aqueous solutions decompose it rapidly. It is insoluble in carbon disulphide, and is decomposed slowly by ethyl ether and glycerol. Sulphuric acid reacts with the liberation of hydrogen sulphide and sulphur dioxide.

The author has attempted to ascertain whether borides of definite composition are present in the materials used in his experiments by decomposing these by treatment with aqua regia. The proportions of the constituents which pass into solution are supposed to indicate oxides of the composition Fe_3B_4 and MnB_3 .

H. M. D.

Preparation of Boron Nitride and Calcium Boride. ALFRED STOCK and WALTER HOLLE (*Ber.*, 1908, 41, 2095—2099).—Boron nitride, although easily prepared, is difficult to obtain in a pure state Stock and Blix, *Abstr.*, 1901, ii, 650; Moeser and Eidmann, *Abstr.*, 1902, ii, 206). It is now found that boron nitride can be prepared by dropping boron bromide into liquid ammonia and gradually heating the resulting boronimide (Joannis, *Abstr.*, 1904, ii, 654) to 750° . Boron nitride, so prepared, reacts only slowly with water, being dissolved in boiling water in one day. In comparison with this, however, phosphorus nitride is highly stable, only about 1% being dissolved by boiling water in two hundred hours. In a glass tube at 180° ,

phosphorus nitride is completely dissolved by boiling water in a few hours, but in this case the alkali of the glass may be concerned.

The action of calcium on boron trioxide leads to the formation of almost pure calcium boride, and not to that of boron, as stated by Moissan (Abstr., 1899, ii, 153). G. Y.

Pure Carbon Dioxide. WALTER P. BRADLEY and C. F. HALE (*J. Amer. Chem. Soc.*, 1908, 30, 1090—1096).—In connexion with a study of the critical state of carbon dioxide (Bradley, Browne, and Hale, Abstr., 1905, ii, 75), it was necessary to prepare the gas in the highest possible degree of purity. A method was therefore devised, and is described in the present paper, by means of which carbon dioxide can be obtained of such purity that only 1 part in 30,000—40,000 parts is incapable of absorption by potassium hydroxide solution. The gas is evolved by the action of pure sulphuric acid on sodium hydrogen carbonate, and special apparatus has been devised for its purification and collection. For details, the description and diagram in the original must be consulted.

In the course of the experiments, it was observed that rubber tubing is slightly permeable to air, even against a pressure of 50 mm. of mercury. E. G.

Tschermak's Method of Preparing Silicic Acids. OTTO MCGEE (*Centr. Min.*, 1908, 325—326. Compare this vol., ii, 277, 499).—A reply to Tschermak. L. J. S.

Preparation of Argon from Air by means of Calcium Carbide. FRANZ FISCHER and OSKAR RINGE (*Ber.*, 1908, 41, 2017—2030).—It is shown that argon can be obtained economically from air by means of calcium carbide. The nitrogen and oxygen are both absorbed when the air is passed over a mixture of calcium carbide (90%) and calcium chloride (10%) heated at 800° in an iron vessel. The nitrogen reacts with the carbide, yielding carbon and calcium cyanamide; the oxygen forms lime and carbon; carbon monoxide and dioxide are also formed, but these ultimately react with the carbide, yielding carbon. The carbide mixture is first heated under reduced pressure in order to remove moisture from the calcium chloride, and then dry air is passed over. The issuing gas contains small amounts of hydrogen, hydrocarbons, and carbon monoxide, and is therefore passed through a vessel containing heated copper oxide. By this process, some 11 litres of argon may be obtained in the course of two days, using about 7 kilograms of carbide.

Details of the apparatus and its use are given. J. J. S.

Percentage of the Inactive Gases in the Atmosphere. A Correction to Previous Calculations. SIR WILLIAM RAMSAY (*Proc. Roy. Soc.*, 1908, 80, A, 599).—The total weights of krypton and xenon in the atmosphere calculated from the volumes (Abstr., 1903, ii, 476) are ten times too small; the true values are 0.028% for krypton and 0.005% for xenon. The values for the proportion of helium and neon previously given (Abstr., 1905, ii, 817) are 100 times too small;

the true percentage of helium is 0.000056 by weight and 0.00040 by volume; of neon, 0.00086 by weight and 0.00123 by volume. G. S.

Preparation of Alcoholic Potassium Hydroxide Solution which will Keep. FRANZ RADE (*Zeitsch. Natur. Genussm.*, 1908, 15, 730—731).—It is recommended that the required quantity of potassium hydroxide should be dissolved in its own weight of water, and the solution, when cold, poured into about 960 c.c. of 95% alcohol, with constant shaking. The whole is then diluted with alcohol to 1000 c.c., mixed, and placed aside until the oily drops of "aldehyde-resin" have separated. The solution is then decanted, and, at the end of about two days, is once more poured off from the separated precipitate (potassium carbonate, &c.). Filtration is unnecessary. W. P. S.

Electrolytic Production of Alkali Chlorates and Perchlorates. M. COULERU (D.R.-P. 195639).—In the ordinary electrolytic processes for chlorates, the production of free alkali hydroxide and hypochlorites diminishes the yield of the required salts. Increased efficiency is gained by the addition of calcium salts, chromates, or dichromates. The addition of chromate may be made in alkaline, neutral, or acid solution, the best effect being obtained in the last case and the worst in the first. Practically, however, the employment of an acid solution has two disadvantages, namely, corrosion of the platinum electrodes and formation of a highly-coloured product. Accordingly, the electrolytic solution is kept neutral by the addition of salts which will interact with any alkali hydroxide to furnish either a hydroxide not affected by hypochlorite, or one which will yield a technically important product when treated with this oxidising agent. Magnesium chloride is the best example of the first type of salt, and lead chloride of the second. In the first instance, the magnesium hydroxide which is precipitated by potassium or sodium hydroxide is not materially affected by hypochlorite, and in the second, the lead hydroxide precipitated by the alkali is oxidised by hypochlorite to lead dioxide. The yield calculated on the current employed is 90% for potassium chlorate and 85% for the corresponding sodium salt.

G. T. M.

Preparation of Anhydrous Sodium Thiosulphate and Hydrosulphide. VEREIN CHEMISCHER FABRIKEN IN MANNHEIM D.R.-P. 194881 and 194882).—Dry pulverulent sodium hydrosulphide results when hydrogen sulphide is passed over sodium sulphide at 60°. If the gas contains carbon dioxide, the sodium sulphide is mixed with the calculated amount of powdered chalk.

Anhydrous sodium thiosulphate is produced by passing oxygen or air over sodium hydrosulphide at 100—150°; it is also formed when sodium sulphide is heated at higher temperatures in a current of hydrogen sulphide and oxygen.

G. T. M.

Preparation of Sodium Perborate. DEUTSCHE GOLD & SILBER SCHNEIDE ANSTALT (D.R.-P. 193732).—A 50% solution of sodium peroxide prepared in the cold is saturated with carbon dioxide and

then treated with a concentrated solution of sodium metaborate. Sodium perborate separates when the liquid is cooled to 2° , providing that sufficient water is present to keep all the alkali carbonate in solution.

G. T. M.

Manufacture of Lithia from Lepidolite. WILLIAM JAY SCHIEFFELIN and THOMAS W. CAPPON (*J. Soc. Chem. Ind.*, 1908, 27, 549—550).—A 97—99% decomposition of lepidolite can be effected by gradually heating a mixture of the ore with 10% more than its weight of sulphuric acid (66° B.) at 340° , the operation lasting about eight hours. The mass is leached with water and the silica separated; the solution is then treated with sufficient potassium sulphate to convert all the aluminium sulphate into alum. After six days, the mother liquor is decanted from the precipitated alum meal. In order to remove the alum still in solution, the liquid is first treated with whiting to neutralise the acid, and then boiled with freshly-precipitated aluminium hydroxide; practically all the alum is thereby precipitated as basic alum or alunite. A subsequent treatment with more whiting removes the last traces of alumina. The solution is then made alkaline with slaked lime and concentrated; it consists chiefly of lithium sulphate, a small amount of calcium sulphate, and traces of manganese and iron oxides. After removal of these impurities, the solution is added to potassium carbonate, and the precipitated lithium carbonate is then washed and dried.

P. H.

Electrolytic Production of Ammonium Persulphate. CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE (D.R.-P. 195811).—Hitherto a good yield of ammonium persulphate has been obtained electrolytically either by the use of a diaphragm or by the addition of a chromate in ammoniacal solution. It has now been found that a saturated solution of ammonium sulphate can be electrolysed so as to give a good yield of persulphate, provided that a current density of not less than 20 amperes per sq. dm. is employed, and that the solution is sufficiently acid not to develop an alkaline reaction in the neighbourhood of the cathode. With a current density of 300 amperes, a yield of 70% of persulphate is obtained without the use of a diaphragm.

G. T. M.

Double Chromates of Ammonium. MAX GRÖGER (*Zellach. anorg. Chem.*, 1908, 58, 412—426. Compare Abstr., 1907, ii, 84, 624).—The compounds in question were prepared almost exclusively by the gradual addition of 10 c.c. of a 2*N* solution of the appropriate salt to 50 c.c. of an approximately 2*N*-solution of neutral ammonium chromate; the precipitate was allowed to remain in contact with the mother liquor for some time, then filtered rapidly, and dried on a porous plate. As many of the salts are decomposed by water, they could not be purified by washing.

Ammonium barium chromate, $\text{BaCrO}_4(\text{NH}_4)_2\text{CrO}_4$, forms light yellow, cubic crystals, and the corresponding *strontium* salt, light yellow, spherical, crystalline aggregates; both are decomposed by water. The corresponding *magnesium* salt, with $2\text{H}_2\text{O}$, forms yellow crystals, and is not decomposed by water.

From zinc chloride and neutral ammonium chromate solution, the compound, $4\text{ZnCrO}_4 \cdot 2(\text{NH}_4)_2\text{CrO}_4 \cdot 3\text{NH}_3 \cdot 3\text{H}_2\text{O}$, was obtained in transparent, dark yellow, spherical granules, but with a chromate containing ammonia in excess, the compound $\text{ZnCrO}_4 \cdot (\text{NH}_4)_2\text{CrO}_4 \cdot 2\text{NH}_3$, already described by Briggs (Trans., 1903, 83, 391), was obtained. Two double salts containing cadmium, of the probable formulae $2\text{CdCrO}_4 \cdot 2(\text{NH}_4)_2\text{CrO}_4 \cdot \text{NH}_3 \cdot 3\text{H}_2\text{O}$ (deep-yellow prisms) and $\text{CdCrO}_4 \cdot \text{NH}_3 \cdot \text{H}_2\text{O}$

(small, granular crystals), were also prepared. When the chromate contains excess of ammonia, the compound $\text{CdCrO}_4 \cdot (\text{NH}_4)_2\text{CrO}_4 \cdot 2\text{NH}_3$ separates in light yellow, prismatic crystals (Briggs, *loc. cit.*). Two mercury salts were also prepared, but their constitution has not been elucidated, and they were probably impure.

With cupric chloride and the chromate containing excess of ammonia, the compound $\text{CuCrO}_4 \cdot (\text{NH}_4)_2\text{CrO}_4 \cdot 2\text{NH}_3$ was obtained (Briggs, *loc. cit.*); with the neutral chromate, the same salt in an impure condition was isolated. With nickel chloride and excess of ammonium chromate, a double salt, $2\text{NiCrO}_4 \cdot 2(\text{NH}_4)_2\text{CrO}_4 \cdot 3\text{NH}_3 \cdot \text{H}_2\text{O}$, has been obtained in small, reddish-brown prisms. Other double salts, obtained by interaction of these two reagents under different conditions, have been described previously. With cobalt chloride, the compound, $3\text{CoCrO}_4 \cdot (\text{NH}_4)_2\text{CrO}_4 \cdot 2\text{NH}_3 \cdot 3\text{H}_2\text{O}$, was obtained in dark reddish-brown granules, readily decomposed by water. With silver nitrate, the compound, $3\text{Ag}_2\text{CrO}_4 \cdot (\text{NH}_4)_2\text{CrO}_4$, was obtained in reddish-brown, granular crystals, and with lead acetate, the compound, $\text{PbCrO}_4 \cdot (\text{NH}_4)_2\text{CrO}_4$, as an amorphous precipitate; both compounds are decomposed by water.

G. S.

The Solubility of Silver Iodide in Ammonia. HENRI BAUBIGNY (*Compt. rend.*, 1908, 146, 1263—1265; *Bull. Soc. chim.*, 1908, [iv], 3, 772—775).—The solubility of silver iodide in aqueous ammonia increases appreciably with rise of temperature. Failure to take this into account is responsible for the discordant results of previous observers. The author shakes known weights of silver iodide (free from chloride) with a definite volume of ammonia in sealed tubes at 50—60°, and, after allowing these to cool to the desired temperature, observes whether or no crystallisation has taken place. In this way, the coefficient of solubility of silver iodide at 16° in aqueous ammonia (D 0.926) is found to be of the order 1/6000, a value considerably lower than that obtained by previous workers.

W. O. W.

Simplest Method of Preparing Carey Lea's Photo-haloids. LÉOPOLD CRAMER (*Zeitsch. Chem. Ind. Kolloide*, 1908, 2, 360—361).—When the halogen salts of silver are allowed to remain in contact, or are warmed, with colloidal solutions of silver, the so-called "photo-salts" are formed. These are separated by dissolving the excess of colloidal silver in nitric acid. The coloured halogen salts are also obtained when a suitable reducing agent is added to silver nitrate which is in contact with the ordinary silver halogen salts. Suitable reducing agents are (1) sodium citrate + ferrous sulphate; (2)

sodium potassium tartrate + ferrous sulphate; (3) tannic or gallic acid + alkali carbonate; (4) formaldehyde + sodium hydroxide; (5) sodium hypophosphite.

The method of preparation described supports the author's view that the coloured salts are adsorption compounds.

H. M. D.

[Preparation of Calcium Hypochlorites.] CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 195896).—When a mixture of 1 part of quicklime and 6.4 parts of water is treated with chlorine until nearly all the lime is used up, a solution is obtained containing 180 to 190 grams of active chlorine and only 1 or 2 grams of chlorate per litre. This solution is then treated anew with lime and chlorine, when crystalline calcium hypochlorite is deposited. This operation may be repeated until nearly all the hypochlorite is precipitated, the action being accelerated by the addition of calcium chloride.

When milk of lime is chlorinated, a point is reached at which further introduction of chlorine does not increase the amount of active chlorine in solution, owing to the formation of basic hypochlorites of the type $\text{Ca}(\text{OCl})_2 \cdot x\text{Ca}(\text{OH})_2$. Two have been isolated in which x is 2 and 4; they cannot be obtained crystalline, owing to the circumstance that they are decomposed by water.

G. T. M.

Colloidal Barium Sulphate. ALBERT RECOURA (*Compt. rend.*, 1908, 146, 1274—1276. Compare Neuberg, *Abstr.*, 1906, ii, 753).—The employment of pure glycerol as a solvent for the reacting salts when barium sulphate is prepared by double decomposition, results in the formation of a stable colloidal variety of the latter substance. The glycerol solution of the colloid can be diluted with several times its volume of water without bringing about precipitation of the insoluble form. The solution is, however, immediately coagulated on boiling. The addition of aqueous solutions of metallic salts (with the exception of mercuric chloride and salts of barium) likewise causes precipitation. Ammonia, baryta, and all monobasic acids, after several hours, bring about a gradual precipitation, whilst polybasic acids (boric acid excepted) cause immediate coagulation. Barium salts increase the stability of the colloid to a marked extent. A solution which has been rendered stable by the addition of barium nitrate can be kept for fifteen days to a month without depositing barium sulphate. Such a solution, however, is immediately coagulated by the addition of salts of polybasic acids; the salts of monobasic acids on the other hand are without action on it.

W. O. W.

Langbeinite and Vanthoffite [$\text{K}_2\text{SO}_4 \cdot 2\text{MgSO}_4$ and $3\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4$]. RICHARD NACKEN (*Chem. Zentr.*, 1908, i, 1850; from *Nachr. K. Ges. Wiss. Göttingen*, 1907, 602—613. Compare *Abstr.*, 1907, ii, 539).—The author has studied the temperature-concentration diagram of the systems MgSO_4 — K_2SO_4 and MgSO_4 — Na_2SO_4 as in previous cases.

1. *Simple sulphates.*—Sodium sulphate and potassium sulphate are enantiotropic dimorphous, with transformation temperatures 24° and 595° , and m. p. 883° and 1076° respectively; they do not

appreciably decompose or volatilise. Magnesium sulphate is considerably decomposed below its m. p., 1124° .

2. *Magnesium sulphate-potassium sulphate system.*—The solidification curve shows a maximum at 33.3 mol. % K_2SO_4 and 936° . Both artificial and natural langbeinite exhibit simple refraction, D^{25}_D 2.829. The eutectic mixture, $MgSO_4$ + langbeinite, m. p. 884° , contains 22 mol. % K_2SO_4 . α - K_2SO_4 in the solid state is miscible with $MgSO_4$ to a limited extent. The eutectic mixture, langbeinite + saturated α - K_2SO_4 mixed crystals, m. p. 747° , contains 62 mol. % K_2SO_4 .

3. *Magnesium sulphate-sodium sulphate system.*—The maximum concentration of this mixture has been found to be $Na_2SO_4 \cdot 3MgSO_4$, m. p. 813° , D^{25}_D 2.0345, double refracting granules, and not as is stated by Le Chatelier, $Na_2SO_4 \cdot 2MgSO_4$. Eutectic mixture, $MgSO_4$ + $Na_2SO_4 \cdot 3MgSO_4$, 808° and 23 mol. % Na_2SO_4 . α - Na_2SO_4 in solid form is miscible with $MgSO_4$ to a limited extent. Eutectic mixture, $Na_2SO_4 \cdot 3MgSO_4$ + saturated α - Na_2SO_4 mixed crystals, 665° and 52 mol. % Na_2SO_4 . Natural vanthoffite shows an alteration in refraction at 489° , and has the same D^{25}_D 2.6955 as the artificial. J. V. E.

Double Chlorides and Bromides of Zinc and the Alkalies.
FRITZ EPHRAIM (*Zeitsch. anorg. Chem.*, 1908, 59, 56–70).—The products obtained by crystallisation of solutions containing chlorides and bromides of zinc and sodium, potassium, ammonium, or lithium at temperatures between about 20° and 100° have been examined.

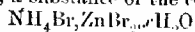
The salt, $2KCl \cdot ZnCl_2 \cdot H_2O$, crystallises from a solution containing a slight excess of zinc chloride. On leaving the mother liquor for some days in contact with the air, the salt, $KCl \cdot ZnCl_2$, separates in thick, monoclinic prisms. Solutions containing potassium chloride in considerable excess, deposit this on evaporation, and later the anhydrous double chloride, $2KCl \cdot ZnCl_2$, appears.

The salt, $KBr \cdot ZnBr_2 \cdot 2H_2O$, crystallises from solutions containing equal molecular proportions of the two bromides in elongated, six-sided tablets. Solutions containing 2 or more mols. of potassium bromide per mol. of zinc bromide yield very fine, hair-like needles of the composition $2KBr \cdot ZnBr_2 \cdot 2H_2O$.

The already-described sodium zinc chloride, $2NaCl \cdot ZnCl_2 \cdot 3H_2O$, is the only double chloride which can be separated.

The salt, $NaBr \cdot ZnBr_2 \cdot H_2O$, crystallises from solutions containing zinc bromide in slight excess in hygroscopic prisms. The salt $2NaBr \cdot ZnBr_2 \cdot 5H_2O$ is obtained in the form of small needles from solutions containing the two bromides in the same ratio.

In addition to the double chlorides and bromides of ammonium and zinc previously described, a substance of the composition



is obtained on evaporation of a solution containing equal molecular quantities of the simple bromides.

On evaporation of a solution containing 2 mols. zinc chloride per mol. lithium chloride, microscopic, six-sided leaflets of the basic salt, $ZnO \cdot 3ZnCl_2 \cdot H_2O$, separate. By slow evaporation of the mother liquor over concentrated sulphuric acid, crystals of the composition $4Cl \cdot ZnCl_2 \cdot 3H_2O$ are obtained. From solutions containing 2 mols.

lithium chloride per mol. zinc chloride, well-formed, hygroscopic, flat prisms of the composition $2\text{LiCl}\cdot\text{ZnCl}_2\cdot 2\text{H}_2\text{O}$ crystallise.

When a solution containing 6 mols. of lithium chloride per mol. of zinc chloride is evaporated on the water-bath and cooled, lithium chloride separates; on repeating these processes until no more lithium chloride crystallises on cooling, a syrupy liquid of the composition $3\text{LiCl}\cdot\text{ZnCl}_2\cdot 10\text{H}_2\text{O}$ is obtained. This liquid, which does not lose water at 100° and does not crystallise when cooled to -20° , is supposed to be a definite compound. The syrupy liquid, after having been kept in a desiccator for about six months, deposited crystals of lithium chloride.

II. M. D.

Rare Earths. HUGO ERDMANN and FRITZ WIRTH (*Annalen*, 1908, 361, 190—217).—The peculiar behaviour of cerium with 1:8-hydroxynaphthalenesulphonic acid (Erdmann and Nieszytko, this vol., i, 621) led the authors to study the salts of this acid with other rare earths, as also the malonates, which, like the oxalates, serve for the recognition and separation of rare metals, since the malonates of the cerium metals are isomorphous and microcrystalline, whilst those of the yttrium earths crystallise in long spears. The sulphides of samarium and gadolinium have also been prepared.

Neodymium and samarium are separated from lanthanum and praseodymium by a long series of fractional crystallisations of didymium magnesium nitrate, $2\text{R}(\text{NO}_3)_3\cdot 3\text{Mg}(\text{NO}_3)_2\cdot 24\text{H}_2\text{O}$, which crystallises in large plates (Demargay, Abstr., 1906, ii, 346). Lanthanum is then separated from praseodymium by Welsbach's method of fractional crystallisation of the double salts with ammonium nitrate. Samarium and gadolinium nitrates were prepared from a euxenite and from the final filtrates from the preparation of neodymium, the samarium being precipitated as the double salt with potassium sulphate, $2\text{Sa}_2(\text{SO}_4)_3\cdot 9\text{K}_2\text{SO}_4\cdot 31\text{H}_2\text{O}$, which crystallises from concentrated potassium sulphate solution. Europium was removed from this precipitate by Urbain and Lacombe's method (Abstr., 1904, ii, 43). The gadolinium which remains dissolved in the potassium sulphate solution was purified by fractional precipitation of the nitrate from nitric acid. The examination of the arc spectra showed that the samarium nitrate was free from neodymium, and therefore from the metals of the cerium group, but contained traces of gadolinium, europium, and yttrium; the gadolinium fraction contained only traces of samarium, dysprosium, terbium, and yttrium.

Malonates of the Rare Earths. As malonic acid does not form precipitates with the salts of the rare earths, malonates were prepared by the action of malonic acid on the hydroxides; on heating the aqueous solutions, the malonates separate in crystalline form. The following malonates are described (compare Holmberg, Abstr., 1907, ii, 90); the figures in brackets are the solubilities in 100 parts of water at 18° : $(\text{C}_3\text{H}_5\text{O}_4)_3\text{La}_2\cdot 5\text{H}_2\text{O}$ (0.0155), white crystals; $(\text{C}_3\text{H}_5\text{O}_4)_3\text{Ce}_2\cdot 5\text{H}_2\text{O}$ (0.0141), white crystals, lose $2\text{H}_2\text{O}$ at 140° , and the remaining $3\text{H}_2\text{O}$ at 180° ; $(\text{C}_3\text{H}_5\text{O}_4)_3\text{Pr}_2\cdot 5\text{H}_2\text{O}$ (0.0179), green, crystalline powder; $(\text{C}_3\text{H}_5\text{O}_4)_3\text{Nd}_2\cdot 5\text{H}_2\text{O}$ (0.0354); $(\text{C}_3\text{H}_5\text{O}_4)_3\text{Sa}_2\cdot 6\text{H}_2\text{O}$ (0.0397), yellow,

granular powder; $(\text{C}_2\text{H}_2\text{O}_4)_3\text{Gd}, 8\text{H}_2\text{O}$ (0.0616), strongly refracting, yellow needles; $(\text{C}_2\text{H}_2\text{O}_4)_3\text{Yt}_2, 5\text{H}_2\text{O}$ (0.1076), white needles;
 $(\text{C}_2\text{H}_2\text{O}_4)_3\text{Er}_2, 10\text{H}_2\text{O}$

(0.1300), long needles. The malonates of the cerium group form prismatic, doubly refracting plates, and effloresce in air; those of the yttrium group form doubly refracting, rhombic needles. All of these salts dissolve in acids, and when boiled with alkalis form the hydroxide of the metal.

8-Hydroxynaphthalene-1-sulphonates of the Rare Earths.—The following 8-hydroxynaphthalene-1-sulphonates were prepared by the action of the acid on the carbonates of the rare metals; they separate from the boiling aqueous solution as heavy powders. The solubilities in 100 parts of water at 14° are given in brackets: $(\text{C}_{10}\text{H}_6\text{SO}_4)_3\text{La}_2$ (0.0926—0.0987), white powder, dissolves in acids, forming bluish-red solutions; $(\text{C}_{10}\text{H}_6\text{SO}_4)_3\text{Pr}_2$ (0.0709—0.0818), green powder, forms bluish-red solutions in acids; $(\text{C}_{10}\text{H}_6\text{SO}_4)_3\text{Nd}_2$ (0.0171—0.0211), grey powder, forms yellowish-red solutions in acids; $(\text{C}_{10}\text{H}_6\text{SO}_4)_3\text{Sa}_2$ (0.0496—0.0573), white powder, soluble in acids; $(\text{C}_{10}\text{H}_6\text{SO}_4)_3\text{Gd}_2$ (0.117), white powder, forms bluish-red solutions in acids;

$(\text{C}_{10}\text{H}_6\text{SO}_4)_3\text{Yt}_2$
 (0.0951), white powder, forms bluish-red solutions in acids;

$(\text{C}_{10}\text{H}_6\text{SO}_4)_3\text{Er}_2$
 (0.0339), white powder. These salts are not hygroscopic, but absorb oxygen, becoming black on exposure to air; when boiled with alkalis, they form metallic hydroxides.

Sulphides of the Rare Earths.—These are best prepared by heating the sulphates in a current of hydrogen sulphide (Muthmann and Stützel, Abstr., 1900, ii, 142).

Samarium sulphide, Sa_2S_3 , forms a yellow mass, D 3.7, burns when heated, forming the oxide and sulphate, is decomposed only slowly by boiling water, and dissolves in acids with evolution of hydrogen sulphide.

Cadmium sulphide, Gd_2S_3 , forms a hygroscopic, yellow mass, D 3.8, and behaves in the same manner as the samarium salt.

G. Y.

Scandium. SIR WILLIAM CROOKES (*Proc. Roy. Soc.*, 1908, 80, A, 116—518).—As the result of spectroscopic examination of fifty-three rare-earth minerals, scandium has been detected in auerite, cerite, keilmaite, mosandrite, orangite, orthite, pyrochlore, thorianite, thorite, and wilkite. All these minerals contain less than 0.01% of scandium, except wilkite, which contains more than 1%.

Wilkite is a black, amorphous mineral, which, when heated to redness in a silica tube, gives off helium, water, hydrogen sulphide, a white sublimate, and traces of hydrogen, carbon dioxide, and neon. An approximate analysis of wilkite gave the following figures: tantalic acid with some niobic acid, 15.91; titanio acid and zirconia, 23.36; earths of the cerium group, 2.55; earths of the yttrium group, 7.64; ceria, 1.17; thoria, 5.51; ferrous oxide, 15.52; uranic oxide, 3.56; silica, 16.98; water and gases, 5.83; calcium, manganese, tin, sulphur, &c., 1.97.

Scandium may be separated by fractional crystallisation from the crude earths, consisting chiefly of yttria, ytterbia, and scandia; its spectrum should be free from the lines of ytterbium.

A number of salts of scandium have been prepared and analysed.

R. J. C.

New Double Salt of Thallium. MORITZ KONS (*Zeitsch. anorg. Chem.*, 1908, 59, 111—113).—When a hot concentration solution of thallous sulphate is added to a solution containing an equal molecular quantity of uranyl sulphate acidified with sulphuric acid, intensely coloured, yellow crystals of the double salt, $\text{Tl}_2\text{SO}_4 \cdot \text{UO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$, belonging to the rhombic system, separate on cooling. Solutions supersaturated with regard to the double salt are easily obtained.

H. M. D.

Freezing-point Diagrams of the Binary Systems, Cu-Cu₂Se, Ag-Ag₂Se, and Pb-PbSe. K. FRIEDRICH and A. LENOUX (*Metallurgie*, 1908, 5, 355—358).—The addition of selenium lowers the freezing point of copper, the eutectic point lying between 2 and 3% Se and 1063°. The curve then rises, soon becoming nearly horizontal. There is some separation into two liquid layers, the limits of which were not determined. The existence of copper selenide, Cu_2Se , melting at 1113°, is demonstrated. Copper does not form solid solutions with selenium.

Mixtures of silver with more than 7% Se separate into two liquid layers. The existence of the selenide Ag_2Se (m. p. between 834° and 850°) is indicated, but mixtures richer in selenium could not be prepared, owing to loss by volatilisation.

Only a single branch of the freezing-point curve of lead-selenium mixtures could be determined. The eutectic point lies close to the lead end. The existence of the compound Pb_2Se , m. p. 1166°, is indicated.

C. H. D.

Non-electrolytic Solution of Mercury in Water and Other Liquids. A. CHURSTOFF (*Zeitsch. physikal. Chem.*, 1908, 63, 346—354).—Experiments show that mercury can dissolve in, and diffuse through, water which contains air, nitrogen, carbon dioxide, sulphuric acid, or potassium hydroxide, as also through benzene, nitrobenzene, and alcohol. The mercury was covered with a layer of water (or other liquid), and the fact of its diffusion was proved by the reduction of a gold chloride solution contained in a separate vessel (compare Barford, Abstr., 1889, 346). In some cases, the mercury was exposed to the air, and the gold chloride solution was protected by a water seal. It is shown, also, that mercury left for a long time in contact with water suffers a slight loss in weight, although no mercury compounds can be detected in the water.

J. C. P.

Two Observations Relating to the Decomposition of Mercuric Iodide. MORITZ KONS (*Zeitsch. anorg. Chem.*, 1908, 59, 10—119).—In alkaline solution, mercuric iodide is decomposed quantitatively by sodium arsenite, with the separation of metallic

mercury. After the solution containing an excess of arsenite has been heated to the boiling point, it is left for several hours, and the separated mercury can then be filtered off. Estimation of the iodide in the solution shows that the reaction is quantitative.

Hydrogen peroxide also liberates metallic mercury from mercuric iodide in alkaline solution. The mercury can be filtered off after one to two hours. The decomposition is not quite complete in this case.

H. M. D.

The Alumino-Silicate, $K_2Al_2SiO_6$. ZYGMUNT WEYBERG (*Centr. Min.*, 1908, 326—330).—Gorgen's method (*Abstr.*, 1890, 13) for preparing the crystalline compound $K_2Al_2SiO_6$ was tried, but better results were obtained by fusing kaolin with a large excess of potassium dichromate. The minute, colourless, isotropic octahedra which result are, however, much contaminated by enclosures of crystallised chromic oxide. Attempts to obtain other salts of the acid, $H_2Al_2SiO_6$, were unsuccessful.

L. J. S.

The Potassium Alumino-Silicate, $K_2Al_2Si_2O_8$. ZYGMUNT WEYBERG (*Centr. Min.*, 1908, 395—402).—By fusing kaolin or a mixture of alumina and silica with a large excess of potassium salts (chloride, carbonate, sulphate, or chromate), a minutely-crystalline product with the composition $K_2Al_2Si_2O_8$ is obtained. The crystals appear to be of two kinds (possibly tetragonal and orthorhombic), and to differ from the hexagonal mineral kaliophilite.

L. J. S.

Preparation of Manganese Compounds. O. DIEFFENBACH (D.R.P. 195523 and 195524).—The reactivity of naturally-occurring manganese dioxide is greatly increased when it is hydrated by heating under pressure at 188° with 30% sodium hydroxide solution. The product which is obtained in a voluminous form contains the hydrate $InO_2 \cdot 3H_2O$.

The decomposition of an alkali manganate in aqueous solution into permanganate, manganese dioxide, and alkali hydroxide can be reversed when manganese dioxide suspended in 30% to 40% potassium hydroxide solution containing a small amount of manganate or permanganate is electrolysed in the anode compartment of an electrolytic cell. When the mixture is stirred and heated, the manganese dioxide is gradually converted into potassium manganate. Instead of manganate or permanganate, a small amount of potassium cyanide may be employed as the oxidising catalyst.

G. T. M.

Alloys of Iron and Carbon. GEORGES CHARPY (*Bull. Soc. chim.*, 1908, [iv], 3, i—xlv).—A lecture delivered before the Chemical Society of Paris, in which a critical résumé of the results obtained in recent years in the study of iron-carbon alloys is given. The following principal lines of investigation are dealt with: (a) deduction of an equilibrium diagram by the application of the phase rule; (b) thermal investigations; (c) isolation of definite constituents from

the alloys by chemical processes; (d) microscopic examination, and (e) observation of the physical and mechanical properties of the alloys. The limits of applicability of each of these methods, and the special difficulties attending the prosecution of each, are discussed, and the bearing of the results obtained by the last four methods of research on the elaboration of a complete equilibrium diagram are considered in detail, and attention is directed to points still requiring investigation. A bibliography of the subject is appended.

T. A. H.

Steels Containing Phosphorus. J. DE KAYLOFF (*Rev. de Métallurgie*, 1908, 5, 355—360).—The brittleness of steels containing small quantities of phosphorus may be removed by quenching in oil and re-heating to 750°. In this way, a uniform structure is obtained if the phosphorus does not exceed 0.07%. A larger proportion of phosphorus prevents the uniform distribution of ferrite and pearlite.

C. H. D.

The Rusting of Iron. J. NEWTON FRIEND (*J. Iron Steel Inst.*, 1908, 77, i, 5—32. Compare Moody, *Trans.*, 1906, 89, 729; *Proc.*, 1907, 23, 84; Tilden, *Trans.*, 1908, 93, 1356).—Boiling pure iron or steel with distilled water in a Jena glass reflux apparatus for two hours does not dissolve any iron. The contrary result of Walker, Cederholm, and Bent (*Abstr.*, 1907, ii, 875) is to be attributed to the retention of some carbon dioxide by the water. An apparatus was devised in which water could be distilled from sodium hydroxide solution on to iron in a closed bulb, and in this case rusting did not take place. In another apparatus, iron was immersed in pure water, and a current of air free from carbon dioxide bubbled through the apparatus. Rusting did not take place if the iron was protected from contact with the glass, although the admission of ordinary air at once caused rusting. It is considered, in agreement with Moody, that the presence of an electrolyte is necessary to the formation of rust. Cast iron rusts even in pure air and water, probably owing to the oxidation of the sulphide and phosphide present. Pure steam is also without action on pure iron at 100°.

Neutral or alkaline hydrogen peroxide is without action on pure iron, although cast iron is rapidly attacked. Pure iron powder, freed from adhering films of gas, is not acted on by pure water at the ordinary temperature.

Neutral salts of the alkali metals exert a corrosive action, and, if the iron is in immediate contact with glass, local corrosion takes place at the point of contact.

C. H. D.

Conductivity of Solutions of Ferric and Ferrous Chlorides and the Structure of Ferric Chloride. WILHELM JEREMIE (*Zeitsch. anorg. Chem.*, 1908, 59, 82—86).—Measurements have been made of the electrical conductivity of concentrated solutions of the two chlorides of iron. The greater conductivity of the ferric solutions at dilutions greater than about 3.6 litres per mol. is interpreted in terms of an opinion expressed by Spring that ferric chloride in solution has the constitution $\text{Fe}_2\text{Cl}_4\text{Cl}_2$. Chlorine is supposed to be ;

set free, and the increased conductivity is attributed to the conversion of this into hydrochloric acid. H. M. D.

Magnetic Oxides of Chromium. IVAN SHUKOFF (*Compt. rend.*, 1908, 146, 1396—1397).—Chromium trioxide decomposes at 330° with loss of oxygen and development of heat. If the decomposition is controlled so that the temperature does not rise above 500° , the oxides obtained are only feebly magnetic. On heating, however, to 500 – 510° , 13–14% of oxygen is evolved, and the black mass, which has the composition $2\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$, is strongly magnetic. An oxide of the same composition, but prepared at 485° , was very feebly magnetic. A crystalline magnetic oxide was obtained by the decomposition of chromyl dichloride; when ignited, it loses only 3.4–4% of oxygen.

W. O. W.

Molybdo-Uranic Compounds. ANDRÉ LANCIEU (*Chem. Zentr.*, 1908, i, 1763—1764; from *Bull. Sci. Pharm.*, 1908, 15, 132—140. Compare *Abstr.*, 1907, ii, 697).—When uranium nitrate is added to an excess of ammonium heptamolybdate and the resulting precipitate boiled with molybdic acid, *uranium heptamolybdate*, $7\text{MoO}_3 \cdot 3\text{UO}_3$, is obtained as an amorphous, yellow powder. It is soluble in all mineral acids, giving a greenish-yellow, fluorescent liquid; it is decomposed by excess of water, and reduced to green uranium molybdate, $\text{U}(\text{MoO}_4)_3$, by alcohol and by acetic acid. The effect of sunlight on the heptamolybdate is to darken its colour, and to render it no longer reducible by alcohol or completely soluble in nitric acid, owing to the formation of insoluble anhydrous *uranium octamolybdate*, $8\text{MoO}_3 \cdot \text{UO}_3$. The hydrated compound, $8\text{MoO}_3 \cdot \text{UO}_3 \cdot 13\text{H}_2\text{O}$, is obtained as prismatic needles when ammonium heptamolybdate is precipitated by uranium nitrate and the product treated with excess of acetic acid; the substance obtained is extremely sensitive to light. A study has been made of the rate of change of this substance when exposed to light of various wave-lengths.

J. V. E.

A New Iodide of Titanium, Titanous Iodide, TiI_2 . EDOUARD DEFAUCQZ and H. CORAUX (*Compt. rend.*, 1908, 147, 65—67).—Titanium tetraiodide (Hautefeuille, *Bull. Soc. chim.*, 1867, [ii], 7, 201) is reducible by silver or mercury to a di-iodide. The reduction is most readily effected as follows: Two porcelain boats, the anterior one containing mercury and the posterior one titanium tetraiodide, are introduced into a porcelain tube and heated gradually in a current of hydrogen to dull redness. A sublimate of mercuric iodide and unchanged tetraiodide is formed in the cooled receiver, whilst fine brilliant black lamellae of *titanous iodide*, TiI_2 , are formed near the exit end of the tube. The crystals, which are very hygroscopic, have D_4^{20} 4.3, are not acted on by organic solvents, are dissolved by concentrated hydrofluoric acid and by boiling hydrochloric acid, forming a blue solution, are violently attacked by nitric and sulphuric acids with loss of iodine, and are decomposed by water and aqueous alkali solutions. Titanous iodide forms additive compounds with dry ammonia and hydrogen chloride. It is reduced by hydrogen at a white heat, but

not at a red heat, giving amorphous titanium, which is very readily oxidised.

The analysis was carried out by the method described previously (Abstr., 1898, ii, 521).
E. H.

Titanium Nitride and a New Class of Titanium Compounds, the Titaniumnitrogenhaloids. OTTO RUFF and FRITZ EISENER (*Ber.*, 1908, 41, 2250—2264).—Wöhler showed originally that a nitride was formed on heating the compound of titanium tetrachloride and ammonia (*Annalen*, 1850, 73, 43), and described four nitrides. Friedel and Guérin (*this Journ.*, 1877, i, 168) reduced this number to two, Ti_3N_2 and Ti_3N_4 . The latter substance has been found by Schneider (Abstr., 1895, ii, 169) to contain less nitrogen than that required by the formula, and he called it nitride A. A reexamination of the substance shows that Ti_3N_4 does not exist. The bluish-black product, obtained by heating the compound $TiCl_4 \cdot 6NH_3$ at the temperature at which Jena glass softens in a stream of ammonia, contains Ti = 72.1, N = 20.77, Cl = 2.64, O = 4.36 (Ti_3N_4 requires Ti = 72.0, N = 28.0). The total titanium was determined by dissolving the nitride in nitric and hydrofluoric acids, and precipitating the titanic acid by ammonia. When the substance is covered with dilute sulphuric and hydrofluoric acids and titrated with N/10 potassium permanganate, the nitride goes slowly into solution as the permanganate is reduced. The solution contains hydrochloric and some perititanic acids; the latter is destroyed by potassium iodide, and the iodine separated estimated by thiosulphate. In this way, Ti, 52.7, was found. As a blank determination with pure TiN gave 76.9 instead of 77.1, the conclusion is drawn that the 52.7 represents the titanium present in the trivalent condition, and, as the chlorine is supposed to exist as TiNCl, the composition of the Wöhler-Schneider nitride is deduced to be TiN = 68, TiNCl = 7.2, $(TiN)_2O$ = 13.5, and TiO_2 = 5.4. When this mixture is heated in a current of ammonia at 1500° for six hours, the chlorine and oxygen are removed completely, and pure bronze-coloured titanium nitride, TiN, is obtained, 101.5. It could not be converted into the chloronitride by chlorine either at 270° or in the liquid state.

An attempt to prepare the nitride, Ti_3N_4 , from the so-called titanamide (Stähler, Abstr., 1906, ii, 595) also resulted in failure. It is also shown that continued extraction of the compound $TiCl_4 \cdot 6NH_3$ with ammonia in a Stock and Blix apparatus (Abstr., 1901, ii, 650), moisture being excluded, does not give titanamide at all, but a titanochloronitride of the composition $Ti_{1.5}Cl_{1.2}N_{0.56}$, 3.5—5 NH_3 , 0.02 TiO_2 . The ammonia is removed by careful heating in a vacuum at 270°, and a dirty green residue of *titanium chloronitride*, TiNCl, is obtained, containing, however, 1.3% nitride and 12—14% titanium oxynitride and titanium dioxide. It is extraordinarily reactive towards water, taking fire and giving ammonium chloride, nitrogen, and titanium dioxide. On further heating, it decomposes, thus: $4TiNCl = 3TiN + TiCl_4 + N$.

Although pure titanium chloronitride was not obtained, the corresponding *bromonitride*, TiNBr, is formed from titanium tetrabromide

(m. p. 39° , b. p. 230°) in a similar manner, the heating of the product obtained on extraction with ammonia being carried out at $200^{\circ}/4$ mm. It also reacts vigorously with water. W. R.

Preparation and Properties of Zirconium Tetrafluoride.

LUDWIG WOLTER (*Chem. Zeit.*, 1908, 32, 606—607).—The method described by Marignac (*Jahresb.*, 1860, 136) for the preparation of zirconium tetrafluoride by heating zirconium dioxide mixed with twice its weight of ammonium hydrogen fluoride, has the disadvantage that this substance volatilises more readily than it attacks the zirconium dioxide. This, however, can be overcome by using, instead of the above mixture, pure zirconium ammonium fluoride, $ZrF_4 \cdot 2NH_4F$, which is readily prepared in a pure state by evaporating zirconium dioxide with excess of silica-free hydrogen fluoride and ammonia, and subliming the product in a platinum tube in a current of nitrogen.

Theoretical yields of the purest zirconium tetrafluoride are obtained by the action of anhydrous hydrogen fluoride on pure zirconium tetrachloride, the change readily taking place in accordance with the equation $ZrCl_4 + 4HF = ZrF_4 + 4HCl$. The product obtained is snow-white, crystalline, and practically insoluble in water. When sublimed, zirconium tetrafluoride forms small, strongly refracting, prismatic crystals having slightly curved facets, D_{20}^{25} 4.4333, and the molecular weight determined by Victor Meyer's method was found to be 166.1, in close agreement with ZrF_4 (166.7). Unlike the other elements of the carbon group, zirconium tetrafluoride is only sparingly soluble in water, 1.388 grams dissolve in 100 c.c. of water without hydrolysis taking place. When warmed to about 50° , the hydrate, $ZrF_4 \cdot 3H_2O$, is precipitated; in no case could any other hydrate or oxyfluoride be obtained. With liquid ammonia, zirconium tetrafluoride gives a white powder ($5ZrF_4 \cdot 2NH_3$), whilst with gaseous ammonia, pyridine, hydrogen sulphide, &c., practically no change takes place. It is suggested that this inactivity of the zirconium tetrafluoride compared with other members of the group is perhaps due to its small molecular volume: TiF_4 , 44.3; ZrF_4 , 37.5; SnF_4 , 40.7. J. V. E.

Oxides of Quinquevalent Bismuth. ALEXANDER GUTBIER and H. MICHELER (*Zeitsch. anorg. Chem.*, 1908, 59, 143—145. Compare Gutbier and Bünz, *Abstr.*, 1906, ii, 174, 234, 551, 678; Ruff, this vol., ii, 298).—The bismuthic acid described by Ruff is entirely different from the substance which is usually referred to by this name in the older literature. In order to avoid confusion, Gutbier and Bünz considered it necessary to retain the name bismuthic acid for a particular product obtained under specified conditions. This substance, which is formed from the dark brown oxidation products (obtained by oxidation of bismuth trioxide in presence of potassium hydroxide solution) by the action of hot concentrated nitric acid, has a colour which varies from scarlet-red to yellowish-red. It has no acid properties, and cannot be obtained from any of the sodium bismuthates which have been described.

In general, the substances obtained by Ruff cannot be compared with those obtained by Guntier and Bünz. This view is expressed as a result of a repetition of Ruff's experiments by the authors.

H. M. D.

Use of Iridium Crucibles in Chemical Operations. SIR WILLIAM CROOKES (*Proc. Roy. Soc.*, 1908, 80, 4, 535—536).—An account is given of the behaviour of pure wrought iridium crucibles during several months' use in ordinary quantitative estimations. Iridium is as hard as steel, and does not blister or alter in weight when repeatedly heated to redness. Heated for some hours in a Bunsen flame with insufficient air supply, the crucible is unharmed, as the deposit of carbon can be entirely burnt away. Sulphur in the gas is also without effect. Boiling aqua regia, fused microcosmic salt, or other phosphates with frequent additions of carbon, strongly heated silica or silicates with a reducing agent, boiling lead at white heat, boiling zinc, and molten nickel, iron, or gold are without effect on the crucible, which, after cleaning, retains its original weight. Fused potassium hydroxide attacks iridium less than platinum, and zinc run in with acid zinc chloride and then heated to boiling only superficially attacks the iridium. Prolonged heating with copper renders the crucible brittle when hot, but the copper can be burnt off. A rhodium crucible is practically as resistant as an iridium one, and has the advantage of being cheaper and only half as heavy.

R. J. C.

Alkali Iridichlorides and Iridiochlorides. MARCEL DELÉPINE (*Compt. rend.*, 1908, 146, 1267—1269).—The iridichlorides of potassium, rubidium, caesium, and ammonium, obtained from sodium iridichloride by double decomposition, conform to the type IrCl_6M_3 . The potassium and sodium salts are black. Large crystals of the ammonium salt are black, but small crystals have a red tint. The rubidium salt varies from brownish-red to brick-red, according to the size of the crystals. The caesium salt, IrCl_6Cs_3 , is bright red and sparingly soluble in water.

The iridiochlorides are readily prepared from the iridichlorides by reduction with a normal oxalate. Thus sodium iridichloride and sodium oxalate yield the very soluble sodium salt, $\text{IrCl}_5\text{Na}_3 \cdot 12\text{H}_2\text{O}$. Aqueous solutions of the potassium and ammonium salts are decomposed by water, thus, $\text{IrCl}_6\text{M}_3 + \text{H}_2\text{O} \rightarrow \text{IrCl}_5(\text{H}_2\text{O})\text{M}_3 + \text{MCl}$; hence to obtain the trimetallic salts excess of an alkali chloride must be added. The crystals which separate are black, brownish-red, green, or yellow, according to size; on dehydration they become olive green. The dimetallic iridiochlorides separate from the mother liquor on concentration. The potassium salt, $\text{IrCl}_5(\text{H}_2\text{O})\text{K}_2$, crystallises in needles; the ammonium salt in octahedra.

Dibutyltin upo-iridio-pentachloride, $\text{IrCl}_5(\text{H}_2\text{O})\text{Rb}_3$, forms small, thick crystals. The caesium salt, $\text{IrCl}_5(\text{H}_2\text{O})\text{Cs}_3$, crystallises in small, olive needles. Trinubidium iridiochloride crystallises in needles containing $11\text{H}_2\text{O}$, and not $12\text{H}_2\text{O}$ as usually represented. The caesium salt, $\text{IrCl}_5\text{Cs}_3 \cdot \text{H}_2\text{O}$, forms bright olive needles.

In accordance with the requirements of Werner's theory for the

constitution of these salts, it is found that the trimetallic salts readily lose their water of crystallisation; the dimetallic salts of the type $\text{IrCl}_3(\text{H}_2\text{O})\text{M}_2$, on the other hand, undergo no change when heated at 150° . W. O. W.

The Preparation of Alkali Iridiochlorides. MAURICE VÉZES (*Compt. rend.*, 1908, **146**, 1392—1393).—A claim for priority (compare Abstr., 1899, i, 572, and Delépine, preceding abstract).

W. O. W.

Mineralogical Chemistry.

An Old Occurrence of Argyrodite at Freiberg. FRIEDRICH KOLBECK (*Centr. Min.*, 1908, 331—333).—A specimen in the A. G. Werner collection at Freiberg was labelled "dunkles Rotgülden," and had been found in 1817 in the Bescheert Glück mine. It is a portion of a large, indistinct crystal with an iron-black colour. On examination, it proved to be the rare mineral argyrodite, in which germanium was discovered. Analysis by T. Döring gave the following results, agreeing with Penfield's formula Ag_8GeS_6 :

Ag.	Ge.	Sh.	Fe.	S.	Total
75.28	6.18	0.36	0.33	17.50	99.65

L. J. S.

Vanadium [Sulphide] from Minasragra. JOSÉ J. BRAVO (*Chem. Zentr.*, 1908, i, 1793; from *Oesterr. Zeitsch. Berg-Hüttenwesen*, 1908, **56**, 166—168).—In an inclined strata of impure carbon of an asphaltic nature, there occur compact masses, 1—2 metres in diameter, composed of a mixture of sulphur, clay, coal-like substances, and vanadium sulphide. The colour of the fresh fracture is pale lead-grey, but the colour rapidly darkens when exposed to the air. An analysis gave:

SiO_2 .	Fe.	Al.	V.	S.	CaO.	Carbon, &c.
22.22	1.68	8.32	15.36	41.81	0.33	10.88

This previously unknown naturally-occurring vanadium sulphide is called *Rizopatovite*; it has 1) 2.456, hardness 3.5, amorphous with a transitory metallic lustre, and is soluble in cold alkali and aqueous ammonia.

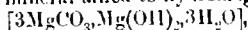
J. V. E.

The So-called Leesbergite. WILLY BRUNNS (*Mitt. Geol. Landesanst. Elsass-Lothringen*, 1908, **6**, 303—307).—This name has been given by Blum (*Ann. Soc. géol. Belgique*, 1907, **34**, *Bull.*, 118—120) to a white, chalky mineral from the Victor iron-mine, between Marspich and Hayingen, in Lorraine; from the analysis (I) he gave, the formula was deduced as $2\text{MgCO}_3, \text{CaCO}_3$. The material

has much the appearance of hydromagnesite; in some parts it is harder and more compact, and in others, softer and looser in texture. In contact with water, the material soon falls to powder, but it does not absorb water as stated by Blum. Under the microscope, it is seen to consist of an aggregate of minute, strongly birefringent grains. Analyses II—IV are of different samples of material dried at 100°:

	CaO.	MgO.	CO ₂ .	H ₂ O.	Insol.	Al ₂ O ₃ + Fe ₂ O ₃ .	Total.
I.	21.06	29.89	49.43	.	0.05	0.52	100.95
II.	16.06	32.81	42.82	[5.17]		3.14	100.00
III.	19.79	29.81	45.85	3.72		0.67	99.84
IV.	15.00	n. det.	46.41	3.19		trace	—

The material is thus not constant in composition, and is without doubt a mixture of a mineral allied to hydromagnesite,



with calcite or dolomite.

L. J. S.

A Chemical Difference between Orthoclase and Microcline. PHILIPPE BARBIER (*Compt. rend.*, 1908, 146, 1330—1332).—Twenty-five orthoclases and five microclines were decomposed by hydrofluoric and sulphuric acids, and the alkali chlorides examined spectroscopically. All the orthoclases contained small amounts of either lithium or rubidium, and sometimes both of these elements were present together, whilst in microcline they were absent. It is therefore considered that orthoclase and microcline are distinct species, and that they may be distinguished by this method.

L. J. S.

[Celadonite from the Færöes.] JAMES CURRIE (*Trans. Edinburgh Geol. Soc.*, 1907, 9, 1—68).—A detailed account is given of the topographical mineralogy of the Færöes. The following analysis, by T. F. Cowie, is given of celadonite from Stigafjall in the island of Strömö. The material lines amygdaloidal cavities in the basaltic rocks, being thicker at the bottom and colouring the associated henlandite up to a certain level in the cavities.

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	H ₂ O	Total.
52.39	26.82	5.00*	1.97	3.05	10.31†	5.72	98.45

* Including FeO.

† Including Na₂O.

At 100° the loss of water is 3.34%, and the remainder is expelled at 180°. This analysis differs considerably, especially in the large content of alumina, from those of material from other localities, suggesting that celadonite or "green earth" is not a definite mineral species.

L. J. S.

Japanese Zeolites. KOTOKI JIMU (*Festschrift zur Mineralogie von Japan*, 1907, No. 3, 115—120).—A description is given of analcite, apophyllite, heulandite, chabazite, and stilbite from Japanese localities. Analysis I, by Tsukamoto, is of optically anomalous crystals of analcite from Maze. [The original paper makes no comment on the fact that this composition is most unusual for analcite; probably there is some error.] It is of large, pale green, optically anomalous

crystals of apophyllite from Maze, where the mineral occurs with analcite, natrolite, and calcite in a basalt-agglomerate. III is of crystals of heulandite from Hatsuneura, in the island of Chichijima; and IV is of sheafs of stilbite from Obara.

	SiO ₂	Al ₂ O ₃	CaO	K ₂ O	Na ₂ O	F	Loss on ignition.
I.	49.67	10.24	12.53	0.99	11.03	—	14.26
II.	50.18	1.33*	26.10	3.16	—	0.95	17.83
III.	60.53	15.67	6.25	0.12	1.51	—	15.98
IV.	54.00	17.94	7.94	—	1.12	—	19.37

* Including a little Fe₂O₃.

L. J. S.

Chlorophyllite from Vizézy. PHILIPPE BARRIER (*Bull. Soc. chim.*, 1908, [iv], 3, 724—725).—A specimen of chlorophyllite from the Vizézy ravine, Montbrison, in the Loire valley, had the following composition:

SiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	K ₂ O	Loss.	Total.
42.43	33.21	10.58	traces	2.61	traces	4.75	6.26	99.87

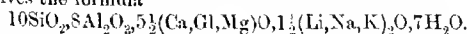
T. A. H.

A New Mineral Occurring with Tourmaline in Madagascar.

ALFRED LACHOIX (*Compt. rend.*, 1908, 146, 1367—1371).—The pegmatite-veins intersecting crystalline limestones and mica-schists in the neighbourhood of Mt. Bity contain in their cavities crystals of smoky quartz, microcline, lepidolite, lithia tourmaline (often of gem quality and in very large crystals, which are often prominently zoned with different colours), beryl, and, in one instance, spodumene (colourless and the violet variety, kunzite). At Maharitra, the pegmatites contain a new mineral, which is described under the name *bityite*. It occurs as small, yellowish-white, hexagonal prisms, which are horizontally striated, and often aggregated in barrel-like shapes, in rosettes, or as a continuous crust over the other minerals. There is a perfect cleavage parallel to the basal plane. D 3.05, H 5½. Optically, the crystals are pseudo-hexagonal, showing a division into six sectors, each with a small angled negative bisectrix perpendicular to the basal plane. The refractive index is 1.62—1.64. Before the blowpipe, the mineral is readily fusible to an opaque, white, blebby glass; it is not attacked by acids. Analysis by F. Pisani gave:

SiO ₂	Al ₂ O ₃	CaO	GlO	MgO	Li ₂ O	Na ₂ O	K ₂ O	H ₂ O	Total.
31.95	41.75	14.30	2.27	0.13	2.73	0.40	0.16	6.50	100.19

This gives the formula



The water is expelled only at a very high temperature, and the formula may therefore be written as $5\text{SiO}_2, 4\text{Al}_2\text{O}_3, 7(\text{R}_2\text{O} + \text{RO})$. The mineral may be classed as a basic orthosilicate in the staurolite and kornepupine group.

L. J. S.

Ilvaite from Shasta Co., California. BASIL PRESCOTT (*Amer. J. Sci.*, 1908, [iv], 26, 14—16).—Massive and crystallised ilvaite occurs at Potter Creek, in Shasta Co., in connexion with ore-bodies of

magnetite at a contact of limestone with diorite. The mineral is of contact-metamorphic origin, and is associated with hedenbergite. The crystals are bright, with a sub-metallic lustre and a greenish-brown streak. The following analysis by H. R. Moss agrees with the usual formula :

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	CaO	MgO	Cr ₂ O ₃	H ₂ O	Total
28.09	0.32	20.80	29.93	3.24	15.89	0.18	0.13	1.62	104.29

L. J. S.

Amount of Dissolved Organic Carbon Compounds in the Sea, and their Significance in its Internal Economy. MARTIN HENZE (*Pflüger's Archiv*, 1908, 123, 487—490; *Zeitsch. allg. Physiol.*, 7, 283, 321; *Abh. K. Ges. Wiss. Göttingen. Math.-physiol. Klasse*, [2], 6, 1).—Pütter has claimed that by the oxidation of the organic matter contained in sea-water, using Messinger's dichromate method, from 18 to 30 mg. of carbon dioxide per 100 c.c. can be obtained, and he stated that the organic matter to which this corresponds serves as nutrition for some of the lower organisms. The author has re-estimated the carbonic acid obtainable by the oxidation of organic matter in sea-water, using antimony for the absorption of the chlorine and other modifications of the Messinger method required in the case of sea-water. He only succeeded in obtaining from 0.4 to 3.5 mg. of carbon dioxide from 100 c.c., quantities which are within the limits of experimental error. He concludes, therefore, that Pütter's hypothesis entirely lacks experimental confirmation. S. B. S.

Physiological Chemistry.

Influence of Oxygen on Respiration. MARCUS S. PEMBREY and F. COOK (*Proc. physiol. Soc.*, 1908, xli—xlii; *J. Physiol.*, 37).—If a person breathes air or oxygen in and out of a spirometer, the breaking point is chiefly determined by the amount of carbon dioxide present. But after exercise, it is easier to breathe oxygen than air in this way, and the breaking point occurs when the amount of carbon dioxide reaches a higher level. This is regarded as supporting the old view that the hyperpnea of muscular exercise is due in part to products of metabolism other than carbon dioxide. W. D. H.

Effects of Excess of Carbon Dioxide and Want of Oxygen on the Respiration and Circulation. LEONARD HILL and MARTIN FLAGG (*J. Physiol.*, 1908, 37, 77—111).—Carbon dioxide at pressures from 15 to 50 mm. causes hyperpnea and convulsive breathing; above 30 to 35 mm. the excitatory effect is transient, and the narcotic effect produced may lead to respiratory arrest. Moderate doses raise the blood pressure and excite the vagus and vaso-motor centres. With higher concentrations, the blood pressure falls, owing to the depressant

effect on the heart. Pure air and massage lead to recovery of the heart. On account of the excitatory effect of the gas, a mixture containing 5% of it should be employed in resuscitating cases of carbon monoxide and nitrite poisoning. The effect of want of oxygen is a dyspnoea much more gradual in onset, and terminating in a convulsive stage of great intensity. The blood pressure is usually, but not always, raised, and the vagus centre is excited, especially in the convulsive stage. The pressure then falls. The heart is not so rapidly depressed as in carbon dioxide poisoning.

The inability to hold the breath depends more on want of oxygen than on excess of carbon dioxide. The power to hold the breath is increased by breathing excess of oxygen. Breathing in and out of a small closed space extends the power to resist alterations in the gases, because the circulation is not mechanically impeded as it is when the breath is held. In muscular exercise, excess of carbon dioxide rather than want of oxygen excites hyperpnoea. Haldane and Priestley are right in stating that normal breathing is regulated by carbon dioxide tension in the alveoli, but in cases of obstructed aëration of the blood, diminished oxygen tension is the more potent agent. W. D. H.

The Residual Nitrogen of the Blood. HERMANN HOHLWEG and HANS MEYER (*Beitr. chem. Physiol. Path.*, 1908, 11, 381—403).—The serum was coagulated in the presence of a mixture of equal parts of 1% acetic acid and 5% potassium phosphate solution, so much of this mixture being added that the resulting liquid was distinctly acid to litmus, but neutral to Congo-red. Before coagulating this acidified mixture, it was diluted, and the diluted liquid half-saturated with sodium chloride. The blood was obtained from the femoral arteries of dogs. In one series of experiments, three samples of blood were withdrawn from each animal at three different periods, the first and last being withdrawn about seven hours after a meal, and the second during a period of starvation. In the second series of experiments, three samples were also withdrawn from each animal, the first and third during a period of starvation, and the second during the height of digestion. The total residual nitrogen was estimated in each sample, as well as that fraction which was precipitable with tannic acid; the urea was also estimated, the methods of Pflüger, Schöndorff, and Mörner-Sjögqvist being employed. It was found, as a mean of all the experiments, that the total residual nitrogen of serum obtained during periods of starvation was 0.0525 gram per 100 c.c., whereas in the serum obtained during digestion it was 0.0788 gram; of these quantities, 0.0384 and 0.0567 gram were due to urea. The fraction precipitable with tannic acid showed no definite relationship to the state of nutrition. There was a small increase of the fraction not precipitable with tannic acid (exclusive of urea) in samples from the well-fed as compared with those from starving animals (0.0130 gram and 0.0060 gram respectively). The increase is too small for any definite conclusions to be drawn as to the circulation of the end products of digestion on the serum. Neither could any very definite increase of such products be detected in the serum after the addition of amino-acids and albumoses to the ordinary diet. S. B. S.

Gürber's Phenomenon. J. DUNIN-BORKOWSKI (*Bull. Acad. Sci. Cracow*, 1908, 318—325).—If red blood-corpuscles saturated with carbon dioxide are placed in a sodium chloride solution, and then removed, it is found that the liquid has become distinctly alkaline (Gürber's phenomenon).

The author has repeated these experiments, and has attempted to measure the concentration of hydroxyl ions by physico-chemical methods, but finds that the concentration is less when the globules have been saturated with carbon dioxide than in the absence of the dioxide.

J. J. S.

The Action of Lipoid-soluble Substances on Red Blood-corpuscles. ISIDOR TRAUBE (*Biochem. Zeitsch.*, 1908, 10, 371—379).—If the theory already advanced as to osmosis (this vol., ii, 565) is correct, solutions with the same surface tension, excepting acids and bases which exert a chemical action, should have the same hæmolytic capacity. Experiments were made to test this theory, and the results seem to confirm it.

Substances which at a certain concentration were found to act hæmolytically, acted anti-hæmolytically below that concentration.

S. B. S.

The Complex Hæmolysins. II. TSUKASAKI (*Biochem. Zeitsch.*, 1908, 10, 345—353).—Urea, the most important final product of metabolism, inhibits lipolysis, acting on the complement, but not on the amboceptor. Thiocarbamide and urethane also exert inhibitory action.

The conception of Sachs and Teruchi that certain sera lose their hæmolytic capacity, owing to the presence of a ferment which destroys the complement at 37° and acts only in the diluted serum, was confirmed by some experiments on dogs' serum. After diluting the serum to 1 in 5, the complement was entirely destroyed by incubating for two hours at 37°.

S. B. S.

Lipolysis, Agglutination, and Hæmolysis. IV. CARL NEUBERG (*Biochem. Zeitsch.*, 1908, 11, 400—403).—An attempt was made to separate a substance producing lipolysis from one producing hæmolysis or agglutination, but without success. The experiments were carried out with ricin and with pancreatic juice. Red blood-corpuscles adsorb the agglutinin; after such treatment, however, the lipolytic function was also lost. Fibrin also adsorbs agglutinin, but a ricin solution treated with fibrin lost its lipolytic properties at the same rate at which it lost its agglutinating properties. Other adsorbents of agglutinins and hæmolysins, such as kaolin, lead to similar results. It seems probable from the experiments that the lipases play an important part in the phenomena of immunity.

S. B. S.

Hæmolysis. SVANTE ARRHENIUS (*Biochem. Zeitsch.*, 1908, 11, 161—171).—Hæmolysis by means of acids was investigated, and it was found that within certain limits there is a minimum action; both by increasing or diminishing the amount of acid above or below

this limit, the hæmolysis is increased. This is due to protein coagulation, which within these limits inhibits the setting free of the hæmoglobin from the corpuscles.

From experiments carried out with suspensions of corpuscles of varying concentration (suspensions of 0.1% to 5%), it was found that the quantity of substance necessary to produce hæmolysis was a linear function of the corpuscle concentration. The corpuscles take up the hæmolysing substance, and hæmolysis follows when a certain relationship exists between the concentration of this substance in the envelopes and that in the surrounding fluid. An equation can be found by means of which the relative quantities of various hæmolysins taken up by the envelopes can be ascertained from experimental data.

Lecithin was found to increase the hæmolytic action of acids, especially if allowed to remain in contact with the corpuscles before the acid was added. It has no action on the hæmolytic power of alkalis, and inhibits that of saponin. Alcohols and ether increase the hæmolytic action of cobra poison, and diminish that of saponin. Sodium oleate increases also the action of cobra poison, diminishing that of saponin. Calcium chloride diminishes the action of the sodium oleate on the cobra poison, this being due, as the author points out, to the formation of an insoluble salt. It is assumed that the lecithin action of acids is due, on the other hand, to increased solubility.

S. B. S.

The Mechanism of Hæmolysis by Saponin. KURT MEYER (*Beitr. chem. Physiol. Path.*, 1908, 11, 357—364).—The hæmolytic action of saponin (Merck) on different species of blood-corpuscles was investigated. It was found that those corpuscles containing the largest amount of cholesterol were most resistant to the hæmolytic action.

S. B. S.

Effect of Diet on the Amylolytic Power of Saliva. C. HUGH NEILSON and D. H. LEWIS (*J. Biol. Chem.*, 1908, 4, 501—506).—Previous results on the influence of diet on animals' saliva are contradictory. The present experiments were performed on human saliva. The amylolytic power rises with carbohydrate, and falls with protein, diet.

W. D. H.

Assimilation of Protein Introduced Parenterally. WILHELM CRAMER. **Assimilation of Protein Introduced Enterally.** HAROLD PRINGLE and WILHELM CRAMER (*J. Physiol.*, 1908, 37, 146—157, 58—164).—Evidence is adduced that egg-white introduced parenterally is partly assimilated and partly eliminated in the urine. The portion which is assimilated is believed to be taken up by the leucocytes. During ordinary absorption from the intestine, the leucocytes are also considered to play an important part. The intestinal mucous membrane is richer in non-coagulable nitrogen than during a fast, and this increase is most marked in the lymphoid nodules of the intestine. The blood of digesting animals shows a

small, but distinct, increase in residual nitrogen over that of fasting animals, and part of this is ascribed to the corpuscular elements.

W. D. H.

Influence on Internal Hæmorrhage on Protein Metabolism. FRED S. WEINOARTEN and BURRELL B. CROWN (*Amer. J. Physiol.*, 1908, 22, 207—244).—Internal hæmorrhage was imitated in dogs by transferring blood to the extent of 2·8 to 3·5 of the body weight from the femoral artery into the abdominal cavity. There was a slight rise of the specific gravity of the urine on the days when this was done, and a very slight rise in the excretion of nitrogen, sulphur, and phosphorus. Many other points in metabolism, secretion, composition of urine, &c., were investigated, but with wholly negative results.

W. D. H.

The Occurrence of Urocanic Acid in a Pancreatic Digest. ANDREW HUNTER (*Proc. physiol. Soc.*, 1908, xxxvii—xxxviii; *J. Physiol.*, 37).—From a long-continued pancreatic digest of plasmin, a substance having the elementary composition and other properties of Jaffe's urocanic acid ($C_{12}H_{12}O_4N_4$) was isolated.

W. D. H.

Relative Rate of Absorption of Optically Isomeric Substances from the Intestine. HENRY D. DAKIN (*J. Biol. Chem.*, 1908, 4, 437—438).—It is well known that isomerides differing in optical action are assimilated to varying degrees by the animal organism. The present experiments performed on intestinal loops with the optically differing lactic acids and other substances gave no evidence of any selection during the preliminary process of absorption.

W. D. H.

Theory of Chemical Energy in the Living Cell. OSCAR LOEW (*Centr. Bakt. Par.*, 1908, ii, 21, 198—200).—Polemical against Bredig (*Abstr.*, 1907, ii, 243).

G. B.

The Difference between Isosmotic and Isotonic Solutions in Artificial Parthenogenesis. JACQUES LOEB (*Biochem. Zeitsch.*, 1908, 11, 144—160).—The first question considered is how a hypertonic solution brings about parthenogenesis. The solution is not so much an exciting as a correcting agent. The excitant is the formation of an artificial membrane of lipid nature (principally lecithin) at the periphery of the egg. The second question dealt with is that isosmotic solutions for the egg are in general not isotonic.

W. D. H.

The Glycogenic Changes in the Placenta and the Fœtus of the Pregnant Rabbit; a Contribution to the Chemistry of Growth. J. LOCHMEAD and WILHELM CRAMER (*Proc. Roy. Soc.*, 1908, 80, B, 263—284).—Analyses were made of the glycogen in the maternal and fetal placenta of rabbits, as well as in the fetal liver and the remaining part of the fetal bodies, which were removed from pregnant animals in different stages of gestation from the fourteenth day

onwards. The placenta was mechanically separated into maternal and foetal parts, and the glycogen in each of these parts was estimated separately. The greater part of the placental glycogen was found in the maternal placenta. It was found that the percentage of this glycogen diminished from the eighteenth day onwards, whereas that in the foetal liver increased. It was also found that there is a distinct parallelism between the growth of the foetus and the amount of glycogen which it contains. The conclusion was drawn that the placenta of the rabbit has the function of depositing glycogen as a store of carbohydrate for the needs of the foetus. The investigation of the distribution of the glycogen-splitting enzyme led to the conclusion that the glycogen is absorbed from the maternal placenta in the form of a simpler carbohydrate, the transformation of the glycogen taking place in the placenta by the action of a secreted enzyme. In the earlier stages of intra-uterine life, the liver of the foetus does not appear to possess the power of storing glycogen; the power is not acquired until the last week of gestation. In the earlier stages of uterine life, therefore, the placenta fulfils the hepatic functions so far as glycogen is concerned. Investigations were also undertaken on the effect of variations of diet and of phloridzin injection, and it was considered from the results obtained that the glycogen metabolism of the placenta and foetus is independent of that by the mother, and is governed by conditions in many respects different from those which regulate the metabolism of the adult animal. The glycogenic metabolism of the rabbit is different from that of the sheep and cow.

S. B. S.

Temperature-coefficient of Rate of Conduction in Nerve. KEITH LUCAS. **Temperature-coefficient of Rate of Conduction and Latent Period in Muscle.** W. J. WOOLLEY (*J. Physiol.*, 1908, 37, 112—121, 122—129).—Maxwell found the temperature-coefficient for conduction in molluscan nerve to be 1.78. The present figures for amphibian nerve give a mean of 1.79. Conduction in amphibian muscle gives a coefficient of 1.79 to 2.01. The conductive process is therefore probably similar in both tissues, but doubt is expressed whether the high coefficient is a necessary proof of a chemical as opposed to a physical process. The coefficient for the latent period of muscle is 3.26 to 3.3; this strengthens the supposition that conduction in muscle is a propagation, not of the contractile change, but of an independent disturbance, which calls up the contractile change at each point on its passage.

W. D. H.

Action of Nitrites and Atropine on Autonomic Nerves. ALFRED FRÖHLICH and OTTO LOEWI (*Arch. exp. Path. Pharm.*, 1908, 59, 14—56).—Certain autonomic nerves can be differentiated from those of sympathetic origin by their behaviour towards drugs, as shown in the following table:

Nerves.	Accelerator.		Inhibitory.	
	Stimulated by	Paralysed by	Stimulated by	Paralysed by
1. Autonomic.....	Pilocarpine	Atropine	Adrenaline	Nitrites.
2. Sympathetic....	Adrenaline	Ergotoxin		

These facts point to chemical differences in the nerve terminals.

W. D. H.

The Permeability of the Frog's Skin. WILLIAM M. BAYLISS (*Biochem. Zeitsch.*, 1908, 11, 226—237).—The physical examination of the frog's skin in the living condition shows that its properties are not so clearly defined as those of the homogeneous membrane of the red corpuscles (Hamburger) or of muscle fibres (Overton). Its properties are only partly explicable on the hypothesis that it is a semi-permeable membrane. Its most interesting property is its reciprocal permeability to sodium ions.

W. D. H.

A New Function of the Pancreas and its Relation to Diabetes melitus. OTTO LOEWI (*Arch. exp. Path. Pharm.*, 1908, 59, 83—94).—In normal men, cats, and dogs, adrenaline does not produce dilatation of the pupil, but this does take place in the following circumstances: (1) After total extirpation of the pancreas in dogs and cats; (2) in pancreatic insufficiency artificially produced in animals; (3) in many cases of human diabetes presumably of pancreatic origin; (4) in many cases of Basedow's disease.

It therefore appears that the pancreas has the power of inhibiting the sensitiveness to adrenalin in certain organs supplied by sympathetic nerves. In the last of the four cases, the susceptibility to adrenaline is possibly produced by hyperthyroidism. W. D. H.

Contraction of Striated Muscle. JOHN S. MACDONALD (*Proc. physiol. Soc.*, 1908, xxv—xxvii; *J. Physiol.*, 37).—An attempt to explain the contraction of muscle by supposing that electrolytes make their appearance in the dark bands which raise the osmotic pressure there, and so water is attracted from the light bands. This is supported to some extent by changes in the distribution of the potassium salts as determined by Macallum's reagent, but the process of relaxation is admittedly left unexplained. W. D. H.

Non-striated Mammalian Muscle. TADASU SAKI (*J. Biol. Chem.*, 1908, 4, 483—496).—The non-striated muscle of the stomach and bladder is richer in water than striated muscle, and contains 2.8% to 3% of nitrogen. Traces of glycogen are present, and only 0.05% of lactic acid, although no precautions to avoid injury were taken. The creatine percentage is also low (0.8%); so is that of creatinine (0.024% to 0.052%). Hypoxanthine is the most abundant purine base; minute amounts of guanine and adenine are occasionally obtained, but never xanthine. The amount of haemoglobin is 0.13% to 0.5%, which is less than in blood-free striated muscle (1% to 2.3%). The amount of connective tissue is greater than in striated muscle. Sodium, iron, calcium, and chlorine are more abundant than in striated muscle; the opposite is true for other elements, potassium, magnesium, &c. There is about three times as much sodium as potassium. The influence of such ions on the manner of contraction is discussed. As much, or almost as much, of the soluble proteins were obtained twenty-four hours after removal in muscles kept at room temperature

as in those kept in ice. No evidence of rigor mortis is therefore forthcoming. In spite of the low percentage of glycogen, evidence was obtained of its disappearance.

W. D. H.

Muscle Plasma. JOHN MELLANBY (*Proc. physiol. Soc.*, 1908, xxxiv—xxxv; *J. Physiol.*, 37).—Muscle plasma, prepared from bird's muscle, and containing 3% of added sodium chloride, clots on the addition of a little acid. This is prevented by dilution with water, but occurs immediately when more salt is added. It is soluble in excess of acid, but this is prevented by adding more salt. The coagulum produced by acid, when thoroughly washed, forms a gelatinous solution in water, which is acid to litmus, and is reprecipitated by small amounts of neutral salts. After careful precipitation of acid, the muscle plasma is practically free from protein.

Wide-reaching conclusions are drawn from these few experiments with salted muscle plasma to explain the coagulation of natural muscle plasma in rigor mortis. The combined action of salt and lactic acid is considered to cause rigor, and the development of more acid to produce its disappearance. The observations are also stated to indicate that there is only one protein in muscle, but in this preliminary communication no evidence is offered on this point.

W. D. H.

The Utilisation of Sugar during Muscular Activity. JOHANNES MÜLLER (*Chem. Zentr.*, 1908, i, 1567; from *Zentr. Physiol.*, 1908, 21, 831—833).—The author has succeeded in isolating lactic acid from the perfusion liquid by means of the zinc salt. In spite of a sufficient oxygen supply, the amount of acid isolated corresponded with the amount of sugar utilised.

S. B. S.

Mono-amino-acids in Meat Extract. KARL MICKO (*Zeitsch. physiol. Chem.*, 1908, 53, 180—211).—Meat extracts contain a small and unimportant percentage of mono-amino-acids (alanine 0·23, glutamic acid 0·08, taurine 0·2%); there is also 0·36% of inosite. Dipeptides were not found.

W. D. H.

A Phytin-splitting Enzyme in Animal Tissues. ELMER V. McCOLLUM and EDWIN B. HART (*J. Biol. Chem.*, 1908, 4, 497—500).—Liver and blood contain a phytase, but not muscle and kidney.

W. D. H.

Influence of Inorganic Colloids on Autolysis. IV. M. ASCOLI and G. IZAR (*Biochem. Zeitsch.*, 1908, 10, 356—370. Compare this vol., ii, 121).—There is in the main an agreement between the action of colloidal silver on metabolism and on autolysis. Minimum amounts favour uric acid production. The uric acid-forming ferments are activated by colloidal silver, ferrous hydroxide, and arsenic sulphide. Larger amounts of the two last named inhibit uric acid formation. Uricolysis is delayed by colloidal silver; the other two colloids have no action on this phenomenon.

W. D. H.

The Autolytic and Hydrolytic Degradation of Protein under Normal and Pathological Conditions. W. GLIXIN and ADOLF LOEWY (*Biochem. Zeitsch.*, 1908, 10, 498—505).—The tissues were allowed to autolyse for several days in toluene water until the action practically ceased. The ammonia-nitrogen, mono-amino-acid nitrogen, and diamino-acid-nitrogen, both in the dissolved part and undissolved part of the tissue, were then determined. The same factors were also determined for a portion of the same tissues which had been directly hydrolysed without previous autolysis. Normal organs were examined (liver and muscular tissue), as well as those from animals which had been poisoned by hydrochloric and hydrocyanic acids. The autolysis of muscular tissue from animals poisoned by acids appears to be somewhat below the normal. The results, however, do not permit of any very definite conclusions being drawn.

S. B. S.

Available Alkali in the Ash of Human and Cows' Milk. JOSEPH H. KASTLE (*Amer. J. Physiol.*, 1908, 22, 284—308).—Although the amount of ash in human milk is much less than in that of cows' milk, the amount of alkali as detected by phenolphthalein, and available for nutritive purposes, is the same. Numerous analyses are given, and various subjects in relation to milk in infant feeding are discussed at length. Among the points raised, the view is acquiesced in that much of the indigestibility of cows' milk in children is due, not so much to its protein constituents, as to excess of fat.

W. D. H.

Milk-serum. FR. LANDOLF (*Biochem. Zeitsch.*, 1908, 10, 486—489).—Fractional examination of the osazones obtained from the serum of cows' milk leads to the conclusion, not that several modifications of lactose are present, but that lactose is united in part to other carbohydrates, and this factor modifies the polarisation, reduction power, fermentation, and the properties of the osazones.

W. D. H.

The Ferment which Destroys Lactose in Milk. ALBERT J. J. VANDEVELDE (*Biochem. Zeitsch.*, 1908, 11, 61—66).—Lactose is gradually destroyed in cow's milk when the latter has not been boiled. The reaction only takes place to a very slight extent in the presence of formaldehyde, but considerable change takes place when the milk is kept sterile by means of iodoacetone. Reducing compounds are formed which have not yet been isolated.

S. B. S.

The Excretion of Sulphurous Acid on the Human Subject after Administration of Sodium Sulphite and Sulphurous Acid in Combination with Sodium Salt. FR. FRANZ and G. SONNTAG (*Chem. Zentr.*, 1908, i, 1477—1478; from *Arch. K. Gesundheits-Amst.*, 1908, 28, 225—260).—Experiments were made to determine the form of excretion of sulphurous acid after administration of neutral sodium sulphite and formaldehyde, acetaldehyde, and dextrose sodium sulphites. Under certain conditions, sulphurous acid was obtained from the urine. This acid can be estimated by

oxidation to sulphuric acid by hydrogen peroxide. Care, however, must be taken in drawing conclusions as to the presence of sulphites in urine, as the latter on distillation yields sulphur compounds of unknown nature. In men, as in dogs, by far the greatest part of the injected sulphite is oxidised to sulphate. In certain cases, after intervals of ten minutes or a quarter of an hour, sulphites can be detected in the urine. The quantity was, however, never more than 1% of the sulphite administered.

S. B. S.

New Organo-mercury Compounds. "Iodoargyrum." GIULIO NARDELLI (*Chem. Zentr.*, 1908, i, 1572; from *Arch. Farm. Sperim.*, 1908, 7, 69—83).—The author finds that the mercury of this compound, $C_4H_4SHg_2I_4$ (Paolini, *Abstr.*, 1907, i, 788), is passed in the urine in larger quantities than in the faeces. Taken in small doses, the iodine is passed in twenty-four hours, and the third constituent, thiophen, could not be detected in the urine; it appears to become changed in the system.

J. V. E.

Estimation of Reducing Substances in Infants' Urine. ROBERTO FUNARO (*Biochem. Zeitsch.*, 1908, 10, 463—466).—The total reduction in normal urine was estimated by Bang's method, the sugar by Bang's method, the uric acid by the Hopkins-Folin method, and the creatinine by Folin's method. After deducting the reduction due to sugar, uric acid, and creatinine, the remainder is due to isomaltose, dextrin, glyconic acid, and unknown substances. Tables of analyses are given, and Larsson's conclusion is confirmed that infants' urine contains a smaller amount of all these substances than the urine of adult men and women.

W. D. H.

Amino-acids in the Urine during Pregnancy. E. C. VAN LEERSUM (*Biochem. Zeitsch.*, 1908, 11, 121—136).—The main difficulty in Pfaunder's method of estimating the amino-acids in urine is the removal of the phosphotungstic salts. They can, however, be entirely removed by the addition of potassium chloride without any loss in the amino-acids taking place. The amino-acid nitrogen varies in health from 2.7 to 7.7% of the total nitrogen. It is increased by administering amino-acids. In pregnant women, it rises to over 10% in 40% of the cases, and the highest point is usually reached just before parturition; in some cases, it occurs after delivery; this may be related to the process of uterine involution.

W. D. H.

Origin of Endogenous Uric Acid. E. PROVAN CATHCART, E. L. KENNAWAY, and JOHN B. LEATHES (*Quart. J. Med.*, 1908, 1, 416—446).—A marked increase in the output of endogenous uric acid is found to occur in three conditions: (a) fever: here the increased output coincides and terminates with the rise of temperature. (b) Exposure to cold. (c) After severe exertion. In the last two cases the increased output outlasts its cause by many hours.

The high output in the morning is not due to retention of uric acid formed during the night (as Hirschstein considers), or to inactivity of the digestive organs in the night (and it is doubtful if

such inactivity really occurs), but to the quickened activity of all functions, especially of voluntary muscles, which occurs after rest. The more lively the performance of the bodily functions the greater does the output of uric acid tend to be, and it is suggested that uric acid has its origin principally in the metabolic processes of the voluntary muscles.

W. D. H.

Creatinine of Infants' Urine. ROBERTO FUNARO (*Biochem. Zeitsch.*, 1908, 10, 467—471).—Creatinine is always present in infants' urine. The individual differences are not great, even if the diet varies. The small amount present explains why those who used the zinc chloride method have been unable to detect it.

W. D. H.

Excretion of Pigments by the Urine. RUDOLF HÜBER and FELICJA KEMPNER (*Biochem. Zeitsch.*, 1908, 11, 105—120).—If pigments insoluble in lipoids were injected intravenously in frogs, they were in part taken up by the kidney colls and excreted. Such pigments are acid magenta, aniline-blue, Congo-red, and many others. Other pigments were not taken up, such as Berlin-blue, benzonazurin, &c. The difference partly depends on how far the pigments are in colloidal solution; those which are not taken up being highly colloidal, but there are exceptions to this rule, for instance, Congo-red.

W. D. H.

Urinary Constituents Precipitable by Phenylhydrazine. HUGO MILRATH (*Zeitsch. physiol. Chem.*, 1908, 56, 126—134).—If dogs' urine is warmed for two hours on the water-bath with phenylhydrazine and acetic acid, phenylsemicarbazide is not obtained. Four to five hours' heating is necessary for the purpose, although cats' urine will sometimes yield the product in two hours. In the case of human urine, two to five hours is necessary, and in ten hours 80% of the urea is converted into phenylsemicarbazide. Aqueous solutions of urea yield similar results.

W. D. H.

Arnold's Urinary Reaction with Sodium Nitroprusside. THEOPHIL HOLOBUT (*Zeitsch. physiol. Chem.*, 1908, 56, 117—125).—In people taking a meat diet, the urine gives a violet reaction with sodium nitroprusside and sodium hydroxide; this soon changes to purple, and finally yellow. If ammonia is used instead of sodium hydroxide, the colour lasts longer. The same coloration is obtained with dogs' urine when the animals are fed on cooked meat, cheese, eggs, and other protein-rich food, but not when they are fed on raw flesh, gelatin, or vegetable albumin.

W. D. H.

Molecular Concentration of Pathological Fluids. ADOLPHE JAVAL (*Compt. rend.*, 1908, 146, 1328—1330).—Hypoconcentration is relatively rare; hyperconcentration is fairly frequent in disease, especially in cases of cardiorenal insufficiency. This is mainly due to salts, and estimations of the amount of sodium chloride in different

fluids of the body are given. The increase of concentration is increased in some cases by the retention of nitrogenous catabolites.

W. D. H.

The Chemical Test for Diseases due to Nerve Degeneration. The Formation of Alkylamines. KOLOMAN BAUER (*Beitr. chem. Physiol. Path.*, 1908, 11, 502—514).—Concentrated urine was, after certain preliminary treatment, made alkaline, and the bases distilled over with steam into acid. The solution of the salts thus obtained was evaporated down and the residue treated with sodium hypobromite, whereby ammonia and primary and secondary bases were destroyed. The tertiary base trimethylamine was then distilled over with steam and isolated in the form of its platinichloride.

It was found that trimethylamine was a constant constituent of normal urine, due to the normal degradation of lecithin substances. Substances containing a choline complex, such as eggs and meat, added to the diet, caused an increase in trimethylamine elimination. The normal output of trimethylamine with a mixed diet is 18 to 26 mg. per day for an adult man. The base was also estimated in several cases of nervous disease. The average quantities found were: 51 mg. daily in the cases of tabes, 59 mg. in myelitis, and 37 mg. in progressive paralysis. In one case of neurasthenia, the amount of trimethylamine found gave no evidence of destruction of nervous matter, whereas in a second case it did. S. B. S.

Protein Metabolism in Cystinuria. CHARLES G. L. WOLF, PHILIP A. SHAFFER [with EMIL OSTERBERG and MICHAEL SOMOGYI] (*J. Biol. Chem.*, 1908, 4, 439—472).—The anomalies of metabolism in cystinuria consist in low ammonia, high undetermined nitrogen, and high neutral sulphur in the urine. The high undetermined nitrogen is partly, and the high neutral sulphur wholly, due to cystine. The ingestion of protein in a cystinuric person increases the neutral sulphur, and so presumably increases the cystine in the urine. If cystine or cysteine is given by the mouth, they are completely broken down to sulphates; it must, therefore, be assumed that the cystine group of the protein is not absorbed as such, but in combination as polypeptide or thio-protocose. These appear to be different types of cystinuria, but it is only in the more severe cases that tolerance for cystine or other amino-acids is diminished. If cystine is given subcutaneously, it is partly oxidised and partly excreted in the urine, but no controls were made on healthy people. Sulphur-free amino-acids are almost quantitatively catabolised to urea. Sodium cholate does not increase the cystine excreted. With regard to the time relations of the excretion after protein-feeding, no standards of comparison in normal persons are at present available. In the cystinuric patients, the maximum of nitrogen excretion occurred later than that of carbon, and the former was coincident with that of sulphur. The maximum excretion of ammonia was early. The curves for neutral sulphur and undetermined nitrogen were approximately parallel. The relationships of cystinuria to bile secretion are discussed, but without any very clear conclusions. In cases of cystinuria in which the excretion of cystine

stops from time to time, the sulphur of the urine returns to normal for these periods, but the undetermined nitrogen remains high on many days; this is possibly due to amino-acids.

W. D. H.

Carbon Dioxide in Venous Blood and Alveolar Air in Cases of Diabetes. ARTHUR P. BEDDARD, MARCUS S. PEMBREY, and EDMUND I. SPRIGGS (*Proc. physiol. Soc.*, 1908, xxxix—xli; *J. Physiol.*, 37).—The results and figures given appear to show that with a prolonged and increasing acidosis in severe diabetes, a point is reached in which increased ventilation of the lungs occurs, which leads to a decrease of the carbon dioxide in the alveolar air and blood, notwithstanding that the blood is still capable, in spite of its reduced alkalinity, of taking up large quantities of carbon dioxide. The increased respiration is ascribed to the stimulation of the respiratory centre by acid substances, including carbon dioxide and other acids produced by metabolism, and prolonged acidosis appears to increase the sensitiveness of the centre.

W. D. H.

Influence of Diuretics on Phloridzin Diabetes. OTTO LOEWI and E. NEUBAUER (*Arch. exp. Path. Pharm.*, 1908, 59, 57--63).—In contrast with other diuretics, the addition of sodium chloride does not increase the diuretic action of phloridzin, neither is the amount of sugar excreted increased by the administration of diuretics.

W. D. H.

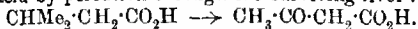
Influence of Calcium on Diuresis. OTTO PURGES and EGON PRIBRAM (*Arch. exp. Path. Pharm.*, 1908, 59, 30--33).—If calcium chloride is introduced into the blood stream, its diuretic action is about equal to that of sodium chloride, unless doses sufficiently large to lower the blood pressure are given.

W. D. H.

Physico-chemical Considerations as to the Pharmacological and Toxicological Actions of Mercury. LUIGI SABBATINI (*Biochem. Zeitsch.*, 1908, 11, 294--310).—The toxic effects of mercury on higher animals, just as in the case of bacteria, as shown by Kronig and Paul, depend on the concentration of mercury ions. Thus, by intravenous injection of sodium chloride, bromide, or iodide before the mercuric chloride, the toxic effect of the latter is depressed, owing to its decreased dissociation due to the presence of the sodium salts. The iodide is more effective than the bromide, and the bromide than the chloride, the iodide and bromide of mercury both dissociating less than the chloride. The lesions due to mercury poisoning can also be explained by the concentration of the mercury ions. These lesions occur chiefly in the secretory and excretory tracts. The concentration of the ions in the saliva, for example, would be great, owing to the absence of chlorides and proteins. In the stomach, on the other hand, the presence of chlorides and of protein would depress the dissociation of the chlorides; here the disturbance in mercury poisoning would be small. In the small intestine, the chlorides and peptones are still in large quantity, and again the dissociation would be small. Still lower in the intestinal tract, owing to absorption of chlorides and products

of tryptic digestion, the dissociation of mercury salts would be greater, and therefore the toxic effects can be observed. The lesions in the kidneys themselves, due to mercuric poisoning, occur almost exclusively in the convoluted tubules. Here, according to the Ludwig hypothesis, the urine is dilute, and becomes gradually concentrated in the passages, and here, also, the dissociation of the mercury salt and concentration of the ions can be great: hence the lesions. S. B. S.

The Degradation of Carboxylic Acids in the Animal Body.
VII. The Formation of Acetoacetic Acid from isoValeric Acid by Perfusion through the Liver. ERNST FRIEDMANN (*Beitr. chem. Physiol. Path.*, 1908, 11, 365—470. Compare this vol., i, 421; ii, 205).—Emhden has shown that isovaleric acid is converted into acetoacetic acid by perfusion through the surviving liver:

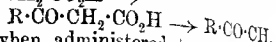


To determine the mechanism of the reaction, perfusion experiments were carried out with the following acids. isoValeric acid, α -hydroxy-isovaleric acid, β -hydroxyisovaleric acid, pyrotartaric acid, and citramalic acid. Of these, only isovaleric acid and the β -hydroxy-derivative lead to the formation of acetone (and acetoacetic acid). From these results, the conclusion is drawn that the secondary carbon atom offers the first point of attack, and that the methyl group is not first oxidised. S. B. S.

The Degradation of Carboxylic Acids in the Animal Body.
VIII. The Behaviour of $\alpha\beta$ -Unsaturated Acids when Perfused through the Liver. ERNST FRIEDMANN (*Beitr. chem. Physiol. Path.*, 1908, 11, 371—375).—Both dimethylacrylic and crotonic acids give rise to acetone by perfusion through the liver, whereas citraconic and mesaconic acids do not. The methyl group here does not offer the first point of attack, but the chemical change can be best explained by assuming that the addition of the elements of water at the double linking first takes place with the formation of β -hydroxy-acids. Dimethylacrylic acid, according to this hypothesis, would be converted into β -hydroxyisovaleric acid, which readily gives rise to acetone (compare preceding abstract). S. B. S.

Degradation of Carboxylic Acids in the Animal Body.
 HENRY D. DAKIN (*Beitr. chem. Physiol. Path.*, 1908, 11, 404—405).—Friedmann has claimed (see this vol., ii, 205, and also preceding abstracts) that, on degradation of carboxylic acids, oxidation takes place first at the β -carbon atom with the formation of β -hydroxy-compounds. To this Knoop has objected, claiming that in normal fatty acids, oxidation generally takes place at the α -position, and that the formation of β -hydroxy-derivatives is an indirect process. Dakin, in support of Friedmann, shows, however, that *n*-butyric acid can yield acetone to the extent of 50% of the theoretical quantity when oxidised by hydrogen peroxide. This reaction can be best explained on the assumption that a β -hydroxy-derivative is first formed. Furthermore, all other fatty acids of the same series, up to stearic

acid, undergo a similar oxidation. Octoic acid yields methyl *n*-amyl ketone; lauric acid, methyl *n*-nonyl ketone, and stearic acid, methyl *n*-pentadecyl ketone. The reactions may be represented as follows:

$$\text{R}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H} \rightarrow \text{R}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}_2\text{H} \rightarrow$$


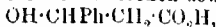
Further, phenylpropionic acid, when administered to an animal, yields, in addition to hippuric acid, β -hydroxyphenylpropionic acid and acetophenone, another example of β -oxidation. The reaction also takes place *in vitro* when hydrogen peroxide is employed as the oxidising reagent (see below).

S. B. S.

The Oxidation of Fatty Acids. FRANZ KNOOP (*Beitr. chem. Physiol. Path.*, 1908, 11, 411—414).—Reply to Friedmann on question of " β -oxidation" (see preceding abstracts of Friedmann and Dakin).

S. B. S.

Oxidation of Phenyl Derivatives of Fatty Acids by the Animal Organism and by Hydrogen Peroxide. HENRY D. DAKIN (*J. Biol. Chem.*, 1908, 4, 419—435).—After hypodermic injection, β -phenylpropionic acid is broken down in dogs to



$\text{COPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, COPhMe , and PhCO_2H , the last substance occurring in the urine as hippuric acid. β -Hydroxy- β -phenylpropionic acid occurs as the levorotatory variety, in close analogy to *l*- β -hydroxybutyric acid. Benzoylactic acid could not be isolated, but its production is inferred from the occurrence of acetophenone in the urine.

The oxidation of β -phenylpropionic acid and of β -hydroxy β -phenylpropionic acid by hydrogen peroxide is very similar, acetophenone and benzoic acid being produced; the oxidation proceeds slowly even at 37°.

In order to test the hypothesis that phenylacetic acid owes its resistance to oxidation to its combination with glycine, β -phenylpropionylglycine, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (thick needles, m. p. 114—115°, more soluble in water than hippuric acid) was synthesised. After administration to dogs, it yields, however, the same degradation products as phenylpropionic acid.

G. B.

[Physiological] Action of Optical Isomerides. III. Adrenaline. ARTHUR R. CUSHY (*J. Physiol.*, 1908, 37, 130—138).—Neutral or *l*-adrenaline acts twice as strongly on the blood pressure as synthetic or *r*-adrenaline, and presumably also on the other organs affected by adrenaline. From this it is inferred that *d*-adrenaline is devoid of action on these tissues, and this was confirmed by the examination of a partly isolated *d*-adrenaline.

W. D. H.

Action of the Digitalis Group on the Kidneys. D. JONASCU and OTTO LOWE (*Arch. exp. Path. Pharm.*, 1908, 59, 71—82).—Substances of the digitalis group act as diuretics in doses insufficient to raise the blood pressure. They act by dilating the renal blood-vessels, and this is a specific effect on these vessels.

W. D. H.

The Action of Strychnine on the Nerve Fibres of the Vagus to the Heart. V. FORLI (*Chem. Zentr.*, 1908, i, 1568; from *Zentr. Physiol.*, 1908, 21, 823—827).—Strychnine sulphate solution was allowed to act on the nerve fibres of the vagus of the heart in a cat; a diminution of conductivity and irritability of the affected position was observed, analogous to the action of the same substance on the sympathetic nerve fibres in the neck. S. B. S.

Sulphurous Acid in its Biochemical Relationship. LEO GRENHUT (*Biochem. Zeitsch.*, 1908, 11, 89—104).—Theoretical considerations are advanced as to the reason of the comparative toxicity of various solutions of sulphites, and compounds with salts of sulphites. The conclusion is drawn that the specific toxicity of a given sulphite solution depends on the quantity of $[H_2SO_3] + [SO_2]$ contained therein. S. B. S.

Chemistry of Phosphorus Poisoning. OTTO PORGES and EGON PÉIBRAM (*Arch. exp. Path. Pharm.*, 1908, 59, 20—29).—In the phosphorus liver, a smaller part of the nitrogen is in the form of protein than in the normal liver. The lessening of hexone bases is still more marked. On autolysis, the nitrogen contained in substances precipitable by tannin is much greater than in autolysis of the normal liver. The nitrogen split off by hydrochloric acid is raised from 10% (the normal number) to 13%. How far these changes are due to differences in ferment action is discussed. W. D. H.

The Supposed Antidotes to Alkaloids and Artificial Antitoxins. H. DORLENCOURT (*Chem. Zentr.*, 1908, i, 1568; from *Bull. Sci. Pharm.*, 1908, 15, 82—88).—The statement of Baudran that antitoxins to alkaloids can be prepared by treating the latter with calcium permanganate was submitted to experimental investigation. It was found that a lethal dose of strychnine, injected intra-muscularly together with the substance produced by the action of calcium permanganate on the alkaloid, produced no toxic action. Heating the mixture to 120° produced no change in its action, and it was found that manganese salts, such as the chloride, act as an antidote to strychnine. There is, therefore, no question of a specific antitoxin. Similar results were obtained by intra-cerebral as by intra-muscular injections, and it is suggested that manganese salts might be employed as antidotes in therapeutic practice. S. B. S.

Cobra Poisoning and Hæmolysis. IVAR BANG (*Biochem. Zeitsch.*, 1908, 11, 520—537).—The importance of lecithin in cobra poisoning, as advanced by Kyes and others, is denied, and the existence of cobra-lecithids considered unproved. Kyes' cobra-lecithid is not a pure substance; it may be a mixture of poison and activator, or a chemical combination, but it is quite uncertain what the activator is; the mixture contains decomposition products of phosphatides, fats, and soaps. Lecithin itself, prepared from egg-yolk, was found to be wholly inactive as an activator to cobra venom in producing hæmolysis; the same is true for the monoamino-

phosphatide, cuorine, and the diamminophosphatide of egg-yolk. The kephalin fraction was found to be active, but the exact composition of this fraction is uncertain. Kossel's protagon, which consists largely of kephalin, is, however, inactive.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

The Action of the Zinc Ion on Media for Microbes. JOSEPH MENDEL (*Compt. rend.*, 1908, 146, 1290--1291).—Two electrodes, one of zinc and the other of platinum, were introduced into an infected gelatin tube, and a current of 1–5 milliamperes was passed through the medium for some minutes. An opaque zone developed round the zinc electrode, and the bacteria with which the medium had been infected grew well everywhere, except within this zone. S. B. S.

Nutrition of Nitrogenous Bacteria. MME. HÉLÈNE KRZEMIEWSKA (*Bull. Acad. Sci. Cracow*, 1908, 445–448).—The presence of potassium salts are essential for the nutrition of nitrogenous bacteria.

Gerlach and Vogel's statement (*Centr. Bakt. Par.*, ii, 10, 636) to the opposite effect is due to the fact that small amounts of potassium salts were always present in the media used in these experiments. J. J. S.

Formation of Acid by the Diphtheria Bacillus. C. LUBENAU (*Arch. Hygiene*, 1908, 66, 305–335).—The production of acid by Löffler's bacillus depends (as is well known) on the presence of carbohydrates in the broth; when the latter is free from carbohydrates, alkali is produced, but only under aerobic conditions. Diphtheroid organisms produce less acid on the whole, and do not form appreciable quantities of alkali. True diphtheria bacilli may produce acid, even in the absence of carbohydrates, if grown in a bouillon in which the proteins have been partly decomposed by a fourteen days' growth of *Bacillus coli*; the acid seems to be derived from the proteins. The addition of glycerol to the culture medium causes the diphtheria bacillus to accelerate its production of acid in the first few days, whilst in the case of diphtheroid organisms the acceleration does not occur until later. G. B.

Part Played by Yeasts in the Aldehydification of Alcohol. J. AUGUSTE TRILLAT and SAUTON (*Compt. rend.*, 1908, 147, 77–80. Compare this vol., ii, 615).—Previous experiments have shown that living yeasts have a greater effect in the formation of aldehyde than yeasts sterilised by heat. Repetition of these experiments, in which the yeast was killed by antiseptics, gave similar results. Thus, living

yeast gave 1100 mg. of aldehyde per 100 grams of alcohol, yeast killed by mercuric chloride gave no aldehyde, that killed by formaldehyde gave traces, whilst after sterilisation by heating at 120°, by means of salicylic acid, and by sodium fluoride, less than 100 mg. of aldehyde were formed. Moreover, increase in the proportion of alcohol present lowers the yield of aldehyde, the alcohol acting as an antiseptic. When yeast cells are killed by the action of chloroform and shaken with 10% alcohol, only traces of aldehyde are produced, and the clear filtrate produced when yeast is crushed in a Berrel apparatus is similarly inactive. If ethyl alcohol is replaced by methyl, propyl, butyl, isobutyl, or amyl alcohol, the corresponding aldehyde is never formed. The proportions of aldehyde and ethyl acetate formed depend on the duration of the experiment; thus immediately after agitation, 1100 mg. of aldehyde, but no ethyl acetate, were found, whereas after four days the amount of acetate was 316 mg., and of aldehyde less than 100 mg. This is probably to be explained by the formation of ethyl acetate from the acetic acid resulting from the oxidation of the aldehyde (compare Kayser and Demolon, *Abstr.*, 1907, ii, 714; this vol., i, 317). It is found, also, that yeasts accelerate the production of ethyl acetate in a solution of alcohol and acetic acid.

The rapid disappearance of the aldehyde previously described occurs only under the influence of living, not of dead, yeasts.

The conclusions are drawn that the production of aldehyde reaches its maximum in presence of the living yeast cell, that it is not effected by the juice contained in the cell, and that the phenomenon is peculiar to ethyl alcohol.

E. H.

Malic Acid in the Production of Wine. Malo-lactic Fermentations. W. MESTREZAT (*J. Pharm. Chim.*, 1908, [vi], 28, 13—20. Compare *Abstr.*, 1907, ii, 903).—The malic acid of grape-juice partly disappears during fermentation, but no lactic acid is formed, and the "malo-lactic" fermentation of Rosenstiehl (*Rev. viticole*, 29, 509) does not exist. During the ripening of the wine, the malic acid undergoes a further slight diminution.

G. B.

The Depression of Fusel Oil Formation, and the Part Played by Bacteria in the Formation of the Higher Alcohols during Fermentation. HANS PRINGSHEIM (*Biochem. Zeitsch.*, 1908, 10, 490—497).—If ammonium sulphate is added as a source of nitrogen, the amount of amyl alcohol formed from leucine is diminished. The addition of 500 and 1000 grams of the sulphate to 2000 litres of mash, diminished the fusel oil yield from 5 to 2 litres; the addition of 250 grams of salt caused a diminution to 2.5 litres. In the fusel oil, *n*-butyl alcohol was found in very appreciable quantities when ammonium sulphate was added to the mash. In the fusel oil obtained when this addition was not made, isopropyl alcohol was found. These alcohols are probably due to the action of bacteria.

S. B. S.

Transformation of Starch in Plants. WL. BUTKEWITSCH (*Biochem. Zeitsch.*, 1908, 10, 314—344).—The change of starch into sugar which is carried out by bark and wood is due to ferment action,

and the diastase was obtained in concentrated form by precipitation of aqueous extracts with alcohol. The bark also inverts maltose. Various conditions, such as changes of temperature on the activity of the ferments, are described.

W. D. H.

The Hydrolytic and Catalytic Ferments Acting during the Process of Ripening of Fruit. GIUSEPPE TALLARICO (*Chem. Zentr.*, 1908, i, 1563—1564; from *Arch. Farm. speriment.*, 1908, 7, 27—48).—Bananas were employed for the study; from this fruit, gathered in different stages of ripening, extracts were made. The catalytic action was determined by investigating the action of the extract on hydrogen peroxide; the amylolytic, by its action on starch; the proteolytic, by the action on gelatin, and the inverting, by the action on sucrose. The following enzymes were present: catalase, invertase, amylase, tyrosinase, and a proteolytic enzyme. The catalytic action is very intense so long as the fruit is green and during ripening; it weakens as the fruit gets black. The amylolytic action takes place when the fruit is green or at the beginning of the stage of ripening; it then disappears. The inverting action is almost entirely absent during the green stage, is intense during ripening, and then gradually disappears. The proteolytic action manifests itself during ripening, and then probably gets weaker.

S. B. S.

Carotene from Carrots and the Substances which accompany it. HANS EULER and ERBA NORDENSON (*Zeitsch. physiol. Chem.*, 1908, 58, 223—235. Compare Willstätter, *Abstr.*, 1907, i, 865; Arnaud *Abstr.*, 1885, 670; 1886, 711; 1887, 859).—When fresh carrots are ground with sand, it is found that the expressed juice contains only a portion of the carotene. The following substances have been extracted from carrots (23 kilos.): Phosphatides, lecithin, &c., 13; dancosterol, 0.5; phylosterol, 1.3; carotene and xanthophyll, 0.7; oil of unknown composition, 3.5 grams. The following method of extraction is recommended: Boil with water, press, dry in absence of air, extract with carbon disulphide, and then with alcohol. Distil, dissolve in small amount of light petroleum, and precipitate the phosphatides with alcohol. The carotene and xanthophyll can be thrown down by the addition of suitable salts to the solution, and can be separated by Willstätter's method.

Dancosterol, $C_{56}H_{102}O_4$ (l), crystallises from boiling alcohol in flocculent masses consisting of microscopic needles, m. p. 283°, and gives the Salkowski-Hesse reaction.

An analysis of the purified phosphatides gave the ratio N : P = 1 : 0.6.

When carotene is oxidised with a small amount of an acetic acid solution of chromic anhydride, rare being taken that the temperature does not rise above 30—40°, an oil, $C_{40}H_{56}O_8$ or $C_{41}H_{56}O_8$, which does not solidify at -10° is obtained. Phytosterol was not obtained when the carotene employed was quite free from this compound.

J. J. S.

The Endo- and Ekto-invertase of the Date. A. E. VINSON (*J. Amer. Chem. Soc.*, 1908, 30, [vi], 1005).—The invertase of the date remains insoluble in all ordinary solvents throughout the green stages,

but becomes readily soluble on ripening, that is, it changes from an endo- to an ekto-form. The change in the behaviour of the invertase towards solvents coincides very closely in point of time with the passage of the tannin into the insoluble form. Evidence is, however, adduced to show that the two phenomena are not causally connected; thus glycerol will dissolve date invertase in presence of soluble tannin, but it fails to extract invertase from green dates. Tannin, however, renders invertase insoluble in water.

It does not appear that the invertase is altered in changing from the insoluble to the soluble form. The rates of inversion of sucrose by equivalent amounts of green and of ripe date pulp are practically identical. Picric acid, chromic acid, and formaldehyde retard the action of green and ripe pulp to approximately the same degree. The living protoplasm does not appear to be directly connected with the inversion, since neither ether, chloroform, nor acetone render inactive the green tissue.

The author explains the difference in solubility by supposing that in the case of the green date the enzyme forms an insoluble compound with some constituent of the protoplasm; on ripening, the protoplasm undergoes profound change, and the enzyme is liberated. He examines and rejects the alternative view, that the cell wall of the green tissue is semi-permeable, whilst that of the ripe tissue is not. E. J. R.

Transitory Presence of Hydrogen Cyanide in Ferns. MAURITS GRESHOFF (*Pharm. Weekblad*, 1908, 45, 770—773).—The author has detected hydrogen cyanide in ferns, such as *Gymnogramme aurea*, *G. lastrea*, and *G. athyrium*. The percentage varied between 0.056 in very young fronds and 0.006 in old fronds, and always diminished with increase in the age of the material examined. A. J. W.

Chemical Examination of Ipomoea purpurea. FREDERICK B. POWER and HAROLD ROGERSON (*Amer. J. Pharm.*, 1908, 80, 251—286).—The chief constituent dissolved by alcohol is a resin, from which by extraction with various solvents the following substances were obtained: pentatriacontane, a phytosterol ($C_{27}H_{46}O$, m. p. 132—133°, $[\alpha]_D -32.1^\circ$, probably identical with sitosterol; compare *Abstr.*, 1903, ii, 517), several fatty acids, a new crystalline alcohol, *ipuranol*, $C_{23}H_{38}O_2(OH)_2$, m. p. 285—290°, and a new acid, termed *ipurolic acid*, $C_{13}H_{25}(OH)_2 \cdot CO_2H$, silky needles, m. p. 100—101°.

Ipuranol yields an *acetyl* derivative, m. p. 160° (not analysed); from the acid, the *sodium* salt, $C_{13}H_{25}(OH)_2 \cdot CO_2Na \cdot H_2O$, the *silver* salt (m. p. 160°), the *methyl* ester, $C_{13}H_{25}(OH)_2 \cdot CO_2Me$, m. p. 68—69°, the *monomethyl ether* of methyl ipurolate, $OH \cdot C_{13}H_{25}(OMe) \cdot CO_2Me$, m. p. 64—65°, and the *diphenylurethane* of methyl ipurolate, $C_{13}H_{25}(O \cdot CO \cdot NHPh)_2 \cdot CO_2Me$,

m. p. 96—97°, were prepared. By decomposition of the various resin fractions with potassium hydroxide and with barium hydroxide, there were obtained a number of acids, including α -methylbutyric acid, $[\alpha]_D +17.95^\circ$, α -hydroxylauric acid, $C_{13}H_{24}O_3$, m. p. 69—70°, and probably azelaic acid. The drug also contains a minute quantity of an essential oil. G. B.

"Bourgou" (*Panicum stagninum*); a Sacchariferous Grass. E. PERROT and EUGÈNE TASSILLY (*Bull. Soc. chim.*, 1908, [iv.], 3, 740—742).—A sample of this grass collected in Upper Senegal was found to contain 10% of sucrose, 7% of reducing sugars, calculated as dextrose, some emulsin, but no invertase or glucosides capable of being hydrolysed by emulsin. T. A. H.

Influence of Manures and Soil Moisture on the Disposition and Perfection of the Ears and the Club Shape of Gottingen Square-head Winter Wheat. W. OHLER (*J. Landw.*, 1908, 56, 153—171; from *Inaug. Diss. Göttingen*, 1907).—The wheat was grown in zinc vessels and pots containing loam, with different manures; the amounts of water were 45% and 70% of the water capacity of the soil.

It is shown that the club shape becomes more marked when the nitrogen supply is increased, whilst a high percentage of moisture in the soil is unfavourable. N. H. J. M.

The Storage and Transportation of Sucrose in the Beet (*Beta vulgaris*). FRIEDRICH STROHMER (*Chem. Zentr.*, 1908, i, 1469—1470; from *Oesterr.-ung. Zeitsch. Zuckerind. Landw.*, 37, 18—21).—In the second year of growth, at the time of flowering, the cane sugar disappears from the roots, and is employed for building up the parts of the plant above the earth. At this time, both in the main stem and in the branches, more invert sugar is found than sucrose, so that hydrolysis into monosaccharides of the latter first takes place, when it is transported, the hydrolysis being followed by re-synthesis. The exposure to light has great influence on the store of sugar; plants which have been kept in the shade half the day during the whole period of growth yield only one-fourth to one-half as much sugar as those which, growing under otherwise similar conditions, have been exposed to full light for the whole day. The plants grown in the shade yielded larger quantities of other products of non-carbohydrate nature, and had consequently considerably less technical value. S. B. S.

Manuring Experiments with Calcium Cyanamide for Potatoes. ALBERT STUTZER (*J. Landw.*, 1908, 56, 141—144).—The potatoes were grown on plots of 100 square metres, without nitrogenous manure, and with 250, 500, and 750 grams of sodium nitrate, "Stickstoffkalk," and ammonium sulphate respectively. Sodium nitrate gave lower yields than "Stickstoffkalk," probably owing to the large amount of rain; the percentage of starch was, however, highest when sodium nitrate was employed. The highest yields per acre of dry matter and starch were obtained on the plot which received 500 grams of "Stickstoffkalk." N. H. J. M.

[Nutritive Value of Non-Proteins in Hay.] MAX MÜLLER (*J. Landw.*, 1908, 56, 192—193. Compare this *vol.*, ii, 220).—The hay extract employed in the feeding experiments previously described (*Abstr.*, 1907, ii, 645) contained 1.87% total N by Jodlbaur's method

and 1.84% by Kjeldahl's. The results obtained with blood-albumin have been confirmed by further determinations. N. H. J. M.

Persistence of the Nitrogen of Green Manure in a Light Sandy Soil. CONRAD VON SEELHORST (*Mitt. deut. landw. Ges.*, 1908, 23, 83—89, 139—144).—Experiments with different plants grown with green manures in a sandy soil in iron boxes having an area of 1 square metre. The nitrogen in the crops was determined, and also the amount per month and nitrogen content of the drainage. The experiments commenced in 1904 (compare *ibid.*, 1906, 21, 289—292, 295—299).

The decomposition of green manure in sandy soil is so rapid that, when applied in October, half the nitrogen may be washed out in the drainage by February or March when the winter has been mild and wet. When applied in February, the decomposition would be still more rapid; the loss of nitrogen is then, however, reduced partly by its being taken up by the growing crop and partly by the amount of drainage being diminished.

The amount of nitrogen was determined in the rain collected in Göttingen in 1906, and the following results obtained:

Rainfall.			Nitrogen.			Rainfall.			Nitrogen.		
mm.			per million. kg. per hec.			mm.			per million. kg. per hec.		
January...	48.7	1.40	0.68			July	124.1	0.72	0.89		
February	47.9	1.40	0.67			August...	79.3	1.26	1.00		
March ...	78.3	0.47	0.37			September	59.7	1.85	1.10		
April	28.9	0.91	0.26			October...	25.1	1.47	0.37		
May	95.6	1.26	1.20			November	53.1	0.84	0.45		
June	84.3	1.25	1.05			December	46.8	1.41	0.66		

The rainfall for the year was 771.8 mm., and the total nitrogen 8.718 kilos. per hectare, or 1.13 per million of rain water.

N. H. J. M.

Action of Organic Nitrogen Manures as Compared with Sodium Nitrate. MAX POPP (*Landw. Versuchs-Stat.*, 1908, 68, 253—300).—Blood meal and horn meal in quantities containing (1) 0.2 and (2) 0.4 gram of nitrogen in each case were mixed with soil (250 grams), and the amounts of nitrogen as ammonia and nitrates determined in water extracts at the commencement and after two, six, and twelve weeks. The following amounts of nitric nitrogen, as percentages of total N, were found:

	At commencement.		2 weeks.		6 weeks.		12 weeks.	
	1	2	1	2	1	2	1	2
Blood meal	0	0	17	8	70	66	72	72
Horn meal	0	0	10	1	54	45	59	57

The amounts of ammonia were very small, except after two weeks, when the nitrogen in that form amounted to 6—13%. Similar experiments, in which calcium carbonate was also added, generally gave very slightly higher results.

Vegetation experiments extending over five or six years are

described, in which different crops were grown successively in large cylinders and manured with a variety of organic manures. The approximate values of the different manures as compared with sodium nitrate were found to be as follows: blood meal and horn meal, 70; fish meal, ricinus meal, and meat meal, 60; Bremer poudrette and bone meal, 55; molasses manure, 40; wool dust, 25, and leather meal, 10.

N. H. J. M.

Gaseous Compounds produced by the Decomposition of Calcium Cyanamide and their Action on Plant Growth. EMIL HASELHOFF (*Landw. Versuchs-Stat.*, 1908, 68, 189—228).—Calcium cyanamide mixed with soil and basalt sand gave off 3.78 and 4.26% of the total nitrogen as ammonia in eight days. In three days, 50 grams of the manure yielded 0.00068 gram of hydrogen phosphide, but no hydrogen sulphide, and in the same length of time 10 grams gave 0.0795% of acetylene.

Results of experiments on germination in presence of the different gases make it probable that the injurious action of calcium cyanamide is due to free ammonia and perhaps also to hydrogen phosphide. Acetylene was found to have no injurious action on germination.

Experiments were also made in soil and water culture on the action of the different gases. The results showed that small amounts of free ammonia, hydrogen phosphide, and hydrogen sulphide are injurious to growth.

N. H. J. M.

Absorption of Calcium Cyanamide in Soil. HUBERT KAPPEL (*Landw. Versuchs-Stat.*, 1908, 68, 301—331).—The absorptive power of soils causes the decomposition of calcium cyanamide into lime and cyanamide. The latter compound is also produced by the action of carbon dioxide, and its production is rapid when both actions occur simultaneously. The formation of cyanamide is favourable to vegetation, since it is more readily attacked by bacteria than the strongly alkaline calcium compound.

In soils of low absorptive power, the transformation of calcium cyanamide is slower, and, under these conditions, injury to germination and plant growth, due to poisonous cyanamide compounds, may occur.

The influence of absorption is only indirect, conditions being produced which are favourable to the rapid conversion of poisonous compounds into harmless substances.

N. H. J. M.

Factors which Influence the Manurial Action of Sparingly Soluble Phosphates. HENRIK G. SODERBAUM (*Landw. Versuchs-Stat.*, 1908, 68, 433—450).—Oats and barley were grown in pots in a sandy soil, deficient in nitrogen and phosphoric acid, manured with different phosphates in conjunction with nitrogen in different forms.

Oats manured with tricalcium phosphate gave slightly lower results with ammonium nitrate and slightly higher results with ammonium sulphate than when sodium nitrate was employed. In the case of barley manured with bone meal, ammonium nitrate caused a similar depression as compared with sodium nitrate, whilst ammonium sulphate

reduced the yield 46.6%. A mixture of sodium nitrate and ammonium sulphate, however, increased the yield (4.1%) as compared with sodium nitrate alone. Tricalcium phosphate, ammonium sulphate, and potassium sulphate gave somewhat higher results (with oats) than when potassium chloride was employed, whilst bone meal, ammonium sulphate, and potassium chloride gave distinctly better results (with barley) than when potassium sulphate was used.

In a subsequent series of experiments, ammonium salts (both nitrate and sulphate) in conjunction with tricalcium phosphate and bone meal respectively considerably increased the yield of oats as compared with sodium nitrate. Barley manured with bone meal and ammonium nitrate gave higher results than with sodium nitrate, whilst tricalcium phosphate and ammonium nitrate gave lower results. Both phosphatic manures (especially tricalcium phosphate) gave much lower results with ammonium sulphate than with sodium nitrate. Addition of equivalent amounts of sodium carbonate to ammonium sulphate in conjunction with bone meal increased the yield of barley, the total produce being then slightly higher (1.1%) than with sodium nitrate and bone meal. In the case of tricalcium phosphate, addition of sodium carbonate with ammonium sulphate nearly doubled the yield obtained with ammonium sulphate and tricalcium phosphate; the yield, however, was still more than 50% below that obtained with sodium nitrate and tricalcium phosphate.

Sodium carbonate in conjunction with ammonium sulphate and phosphates very slightly reduced the yield of oats as compared with ammonium sulphate and phosphates alone.

The changes in the physiological reaction caused by different nitrogenous compounds will not only vary with different plants, soils, and with different amounts and kinds of the other manures employed, but may even be reversed.

N. H. J. M.

Analytical Chemistry.

Absorption Bulbs for use with Bottles containing Standard Solutions, &c. M. EMMANUEL POZZI-ESCOT (*Bull. Assoc. chim. Agr. Dist.*, 1908, 25, 1077).—A piece of apparatus is described which may be fitted to bottles containing standardised alkali solutions in order to prevent the entrance of carbon dioxide, &c., to the bottle when the solution is drawn off into a burette. It consists of a bulb provided with a side-tube reaching to the bottom of the bulb; the air enters by this tube and, after bubbling through potassium hydroxide solution or other absorbent placed in the bulb, leaves through a tube at the top of the bulb. This tube is bent downwards so that it can be fixed through a hole in the cork of the bottle. By slightly altering its form, the bulb may be used to absorb the gases formed during fermentation experiments, and for other purposes.

W. P. S.

Replacement of Hydrogen Sulphide in Chemical Analysis. EDUARD DONATH (*Chem. Zeit.*, 1908, 32, 629—630, 645—647).—The author recommends the process used by Vortmann chiefly on hygienic grounds.

This process is, briefly, as follows: the solution is made alkaline with sodium hydroxide and then heated with excess of pure sodium sulphide, which dissolves the metals of the tin group. The insoluble matter is then treated with dilute hydrochloric acid, which dissolves all but the sulphides of those metals which are precipitated in the usual course with hydrogen sulphide; cobalt and nickel are also left undissolved. For further details, Vortmann's brochure is referred to.

In order to prepare ammonium sulphide without using a hydrogen sulphide apparatus, distillation of sodium sulphide with ammonium chloride solution is recommended.

L. DE K.

Use of Certain Organic Acids and Acid-Anhydrides for the Standardisation of Alkali and Acid Solutions. ISAAC K. PHELPS and L. H. WEED (*Zeitsch. anorg. Chem.*, 1908, 59, 114—119).—Experiments are recorded which show that succinic acid, succinic anhydride, malonic acid, benzoic acid, phthalic acid, and phthalic anhydride can be used, with phenolphthalein as indicator, for the titration of sodium and barium hydroxide solutions with the same degree of accuracy as a solution of hydrochloric acid standardised by precipitation with silver nitrate.

H. M. D.

Comparison between Succinic Acid, Arsenious Oxide, and Silver Chloride for the Standardisation of Solutions in Iodimetry, Alkalimetry, and Acidimetry. ISAAC K. PHELPS and L. H. WEED (*Zeitsch. anorg. Chem.*, 1908, 59, 120—126. Compare preceding abstract).—Succinic acid can be accurately employed for the standardisation of sodium thiosulphate solutions. The authors' method consists in standardising a pure sodium hydroxide solution by means of succinic acid. This solution is used to titrate a solution of a mineral acid, a known quantity of which is added to an excess of solution containing potassium iodide and iodate. The thiosulphate solution is then used to titrate the liberated iodine. Results quite as accurate as those yielded by the estimation of iodine with a standard arsenious oxide solution are obtainable. The liberation of iodine by mineral acids from an iodide-iodate solution is not complete in very dilute solution.

H. M. D.

Separation of Chlorine, Bromine, and Iodine by means of Hydrogen Peroxide in Acid Solution. PAUL JANNASCH (*J. pr. Chem.*, 1908, [ii], 78, 28—34).—In continuation of the study of the separation of the halogens by means of hydrogen peroxide, a method has been worked out for the quantitative separation of chlorine, bromine, and iodine from each other. The haloid mixture is made acid with acetic acid and treated with hydrogen peroxide; the iodine is then distilled off in a current of carbon dioxide, collected in an

aqueous solution of ammonium hydroxide and hydrazine sulphate, and estimated as described previously (Abstr., 1906, ii, 194). The bromine and chlorine in the distillation residue are separated and estimated as before (Abstr., 1906, ii, 894), with the difference that the bromine is collected in a solution of sodium, instead of ammonium, hydroxide and hydrazine sulphate. The analyses quoted show that the method gives good results for chlorine and iodine, but that bromine is found slightly too low.

G. Y.

Detection and Estimation of Chlorites and Hypochlorites in Chlorates. BIRGER CARLSON and JULIUS GELHAAR (*Chem. Zeit.*, 1908, 32, 604—605, 633—634).—*Qualitative Examination of Chlorates.*—Five grams of the sample are dissolved in 100 c.c. of cold water and a drop of zinc iodide-starch solution is added. If no immediate blue colour is noticed, hypochlorites are absent. Two c.c. of $N/10$ sulphuric acid are now added, and if there is no immediate coloration, neither hypochlorites nor chlorites are present. These directions must be strictly adhered to.

Quantitative Estimation.—The following is an outline of the method employed: The hypochlorite is titrated in the usual manner with arsenious acid, the excess of which is then titrated with iodine. To another portion of the solution is now added the requisite amount of arsenic solution to destroy the hypochlorite, and, after diluting to 250 c.c. and heating to 95° , the solution is titrated as quickly as possible with indigo solution; if neutral or alkaline, the liquid should be acidified faintly with dilute sulphuric acid. The indigo solution is prepared by dissolving about 6 grams of sodium indigotinsulphonate in a litre of water, and should be checked with a solution of chlorite, checked in turn with standard iodine and thiosulphate. L. DE K.

Estimation of Sulphur in Iron and Steel. MAX ORTHEY (*Zeitsch. angew. Chem.*, 1908, 21, 1359—1364, 1393—1399).—The following published processes may be recommended. They are all based on the evolution of the sulphur as hydrogen sulphide and absorption of the latter in cadmium acetate solution; the cadmium sulphide is converted by means of copper sulphate into copper sulphide, which is then burnt to oxide (1, 2, 3, 4), or the cadmium sulphide is estimated iodometrically (5, 6):

(1) The sample is treated with hydrochloric acid, D 1.19. (2) The gases are passed through a red-hot tube. (3) The hydrochloric acid fumes are condensed in a little water, which is afterwards boiled to expel any hydrogen sulphide. (4) A mixture of zinc and cadmium acetate is used. (5) An ammoniacal solution of cadmium acetate is used. (6) An acetic acid solution is employed.

In the case of steel, the following methods may be used also: (7) The sample is dissolved in dilute hydrochloric acid (1:2), and the gases passed through a red-hot tube. (8) Acid, D 1.124, is used, and the gases ignited. (9) The same, but a mixture of dilute hydrochloric acid (1:2) and dilute sulphuric acid (1:4) is used instead. For reference, analyses 3, 4, 5, and 6 should be used.

Good results are obtained also by the following methods, where the sulphur is finally weighed as barium sulphate: (a) The sample is dissolved in strong hydrochloric acid, and the heated gases are passed through ammoniacal hydrogen peroxide. (b) The sample is oxidised with nitric acid, D 1.42, the nitric acid is expelled by excess of hydrochloric acid, and the ferric chloride removed by shaking with ether; or the iron is precipitated with ammonia, and, after adding barium chloride, the ferric hydroxide is re-dissolved by hydrochloric acid. (c) The iron is treated with copper-ammonium chloride, and the residual matter oxidised with nitro-hydrochloric acid and potassium chlorate.

L. DE K.

Decomposition of Certain Minerals and Industrial Products by means of Sodium Peroxide and Metallic Sulphides. JAMES H. WALTON, JUN., and HERMAN A. SCHOLZ (*Amer. Chem. J.*, 1908, 39, 771—789).—A method is described for decomposing certain mineral substances, and is particularly applicable to sulphide ores and products containing a large proportion of silica, such as glazes and slags. The decomposition is effected by fusing the material in a nickel crucible with a mixture of sodium peroxide, zinc sulphide, and potassium persulphate. In the case of basic substances, such as franklinite and chrome iron ore, iron pyrites is added in order to increase the temperature.

The method yields accurate results, and is very rapid; the silica is brought into solution, and therefore does not tend to clog the filters, and the use of platinum crucibles is obviated.

E. G.

Colorimetric Estimation of Phosphorus in Steel. G. MISSEN (*Chem. Zeit.*, 1908, 32, 633).—The reagents required are (1) Pure nitric acid, D 1.2. (2) Potassium permanganate, 8 grams per litre. (3) Pure hydrogen peroxide, prepared by introducing gradually 40 grams of sodium peroxide into a cold mixture of 900 c.c. of water and 100 c.c. of nitric acid. (4) Ammonium vanadate, prepared by dissolving 2.345 grams of the salt in 500 c.c. of water, adding 20 c.c. of nitric acid, and diluting, when cold, to one litre. (5) A freshly-prepared 10% solution of ammonium molybdate.

One gram of the sample is dissolved in 20 c.c. of reagent (1), and boiled and mixed with 10 c.c. of reagent (2). After boiling a few seconds longer, 10 c.c. of reagent (3) are added to redissolve the manganese precipitate, then 10 c.c. of reagent (4), and the excess of peroxide is removed by boiling. When cold, the liquid is diluted to 60—65 c.c., 10 c.c. of reagent (5) are added, and the whole is diluted to 800 c.c. exactly. After two or three minutes, the coloration is compared with that of a standard sample treated similarly; the colour is stable for several days.

L. DE K.

Estimation of Phosphoric Acid in Foods. EMIL WORSER (*Zeitsch. Nahr. Genussm.*, 1908, 15, 732—734).—According to the process described, the organic matter of the food is destroyed by heating with sulphuric and nitric acids, the phosphoric acid is then precipitated by the addition of ammonium molybdate solution, and the amount of phosphoric acid in the precipitate is estimated volumetrically.

From 1 to 5 grams of the dry sample are heated in a flask with 5 c.c. of concentrated sulphuric acid and 5 c.c. of nitric acid until the nitric acid has been expelled and fumes of sulphuric acid are evolved. If the remaining solution is dark in colour, a little more nitric acid is added and the heating continued. The solution is cooled, diluted with 20 c.c. of water, boiled for a short time, and filtered to remove silica and any trace of undecomposed fat. The filtrate, amounting to 100 c.c., is then treated with 30 c.c. of 50% ammonia, heated to a temperature of about 80°, and 25 c.c. of 10% ammonium molybdate solution are added. The mixture is shaken for a short time and, after the lapse of fifteen minutes, filtered, and the precipitate washed with water by decantation until free from acid. The filter is next placed in the flask containing the precipitate, 150 c.c. of water are added, a measured quantity of $N/2$ sodium hydroxide solution (about 5 c.c. more than is required to dissolve the precipitate) is introduced, and the contents of the flask are boiled until all the ammonia has been expelled. The excess of sodium hydroxide is then titrated back, using phenolphthalein as indicator. Each c.c. of $N/2$ sodium hydroxide solution is equivalent to 0.001268 gram of phosphoric anhydride or to 0.000556 gram of phosphorus.

W. P. S.

Estimation of Phosphates in Urine. ANNIBALE FERRARO (*Boll. chim. farm.*, 1908, 47, 399—400).—In the estimation of phosphates in urine by Neubauer's method, the uranium solution must be run in in drops throughout, with brisk agitation, the solution to be tested being kept at the temperature of the boiling-water bath. The last reading should be taken after six to seven minutes of rapid stirring. When much calcium phosphate is present, it is better to run the solution to be tested from a burette into the uranium solution. Potassium ferrocyanide is to be preferred to cochineal as an indicator.

C. H. D.

The Dyer Method for the Determination of Plant Food in Soils. FRANK T. SHUTT and A. T. CHARRON (*J. Amer. Chem. Soc.*, 1908, 30, [iv], 1020).—Experiments are recorded showing the effect of (1) the time of digestion and (2) the volume of the solvent in making analyses of soil by Dyer's method (*Trans.*, 1894, 65, 115). The authors used a rich black loam from the prairie at Tisdale, Sask., described as typical of large areas in the Canadian north-western wheat belt, and characteristically rich in nitrogen and organic matter. Four sets of determinations were made: samples weighing 100 grams of soil were extracted for (a) seven days, (b) five hours, with 1000 c.c. of 1 per cent. citric acid, and (c) seven days, (d) five hours, with 500 c.c. of 1 per cent. citric acid; the results were:

		P_2O_5 , per cent.	K_2O , per cent.	CaO , per cent.
Seven day digestion, 1000 c.c. solvent	(a) ...	0.02287	0.03818	0.5320
" " " 500 c.c. "	(c) ...	0.01999	0.03355	0.2718
Five hour digestion, 1000 c.c. "	(b) ...	0.01807	0.03958	0.5210
" " " 500 c.c. "	(d) ...	0.01599	0.03089	0.2285

A reduction in the volume of the solvent has materially reduced the percentages of phosphoric acid, potash, and especially of lime

obtained; reduction in the time of digestion has caused a falling off in the amount of phosphoric acid, has scarcely affected the lime, and not at all the potash. It is evident that the volume of the solvent is a more important matter than the time of digestion.

E. J. R.

Detection of Arsenic in Urine. ERNST SALKOWSKI (*Zeitsch. physiol. Chem.*, 1908, 53, 95—114).—The paper is mainly concerned with methods for oxidising the urine prior to the application of Marsh's test. The method recommended is to oxidise the evaporated alcoholic extract of the urine by treatment with 15 c.c. of nitric acid (D 1.48), and then to heat the mixture with 10 c.c. of sulphuric acid in a Kjeldahl flask, occasionally adding 0.5 c.c. of nitric acid until oxidation is complete. Various other practical details are discussed.

G. B.

Iodometric Estimation of Arsenic and Antimony in the Presence of Copper. F. H. HEATH (*Amer. J. Sci.*, 1908, [iv], 513—519; *Zeitsch. anorg. Chem.*, 1908, 59, 87—93). The solution, which must contain the arsenic or antimony in the higher state of oxidation, is mixed with 1–2 grams of citric acid and then with potassium iodide (3 grams to 50 c.c., 5 grams to 100 c.c.). The iodine liberated, which represents the copper, is then titrated with standard thiosulphate. The filtrate from the cuprous iodide is treated with 1 c.c. of bromine and boiled in order to expel the iodine, if necessary with further addition of bromine, which is then in turn boiled off completely. The whole is now diluted to 100 c.c., and, after adding 2 grams of potassium iodide, the solution is boiled down to half its bulk. When cold, any free iodine is decolorised with sulphurous acid, using starch as indicator. After diluting again to 100 c.c., iodine solution is added until the liquid is coloured, and then very dilute sulphurous acid to make the colour disappear. Excess of sodium hydrogen carbonate is now added, and the arsenic or antimony titrated with standard iodine in the usual way.

When both arsenic and antimony are present, the copper estimation is not quite so satisfactory.

L. DE K.

Parr's Method of Determining the Heat of Combustion of Coal. EMIL J. CONSTAM (*Zeitsch. angew. Chem.*, 1908, 21, 1414).—Polemical. A reply to Parr (this vol., ii, 533).

P. H.

Volumetric Estimation of Carbon Dioxide and other Acids in Air. H. HENRIET and M. BOUYSSE (*Compt. rend.*, 1908, 146, 1100—1101).—The air is passed through standardised sodium or potassium hydroxide solution, and the latter is then diluted to a definite volume. One-half is next titrated with acetic acid, using phenolphthalein as indicator, and the decrease in titre of the solution multiplied by 2 is equivalent to the amount of carbon dioxide in the air; the neutral point is reached when the normal carbonate formed has been converted into hydrogen carbonate. The second half of the solution is then treated with barium chloride, and titrated with acetic acid without removing the barium

carbonate. The quantity of alkali required to neutralise the total acidity of the air is thus obtained, and the amount of the acids other than carbon dioxide may be calculated.

W. P. S.

The Autolysator, an Apparatus for the Automatic Estimation of Carbon Dioxide. CHARLES A. KEANE and HARRY BURROWS (*J. Soc. Chem. Ind.*, 1908, 27, 608—610).—The apparatus is used for the automatic analysis of furnace gases. The absorption of the carbon dioxide is effected by means of soda-lime, and the pressure of the gas before and after the absorption is measured by differential manometers. The gas to be analysed is drawn by water suction of constant pressure through two similar capillary tubes, each of which is connected with a manometer. By interposing the absorbent substance between the two capillaries, the difference in pressure due to the absorption of the carbon dioxide is indicated on the manometer, provided that the flow of gas be so regulated that a constant volume flows through the apparatus. A full description, with diagrams, of the apparatus is given in the original paper.

W. P. S.

Application of the Cobaltinitrite Method to the Estimation of Potassium in Soils. W. A. DRUSHEL (*Zeitsch. anorg. Chem.*, 1908, 59, 97—101. Compare this vol., ii, 66).—The method already described is applied to the estimation of potassium in soils. A weighed quantity of soil is extracted on the water-bath with 20% hydrochloric acid. The acid is then removed by evaporation, and the bases separated by addition of sodium carbonate or ammonia and ammonium oxalate. After removal of the ammonium salts and the organic matter by heating to redness, the residue is dissolved in water, acidified with acetic acid, and evaporated with excess of sodium cobaltinitrite. The further procedure is exactly the same as that previously described (*loc. cit.*).

H. M. D.

Estimation of Lead in Alloys. W. ELBORNE and C. M. WARREN (*Chem. News*, 1908, 98, 1).—One gram of the alloy in fine shavings is put into a flask with 50 c.c. of hydrochloric acid, and a slow current of chlorine is passed for twenty-four hours. When all is dissolved (sometimes heat must be applied towards the end), the solution is transferred to a small weighed porcelain dish, evaporated to dryness on a water-bath, and the residue cooled in a desiccator.

The mass is then treated repeatedly with absolute alcohol; this dissolves all the chlorides present except the lead chloride, which is then dried at 100° for three hours and weighed. For fear any lead chloride may be lost, the filtrate and washings are passed through a weighed filter, which is then also dried at 100°.

L. DE K.

Rapid Valuation of Pastilles of Mercurio Chloride and Cubes of Sodium and Potassium Iodides. PAOLO FIORA (*Boll. chim. Farm.*, 1908, 47, 401—402).—The mercuric chloride pastille (1 gram) is dissolved in water, and a solution of 1.162 grams of potassium iodide added. After filtering, a 1% solution of mercuric

chloride is added, the formation of a precipitate indicating a deficiency in the pastille. The quantity given allows a margin of 0.05 gram. For 1 gram cubes of potassium and sodium iodides, 0.776 and 0.859 gram of mercuric chloride are added respectively, a very dilute solution of potassium iodide being used for titrating back.

C. H. D.

Estimation of Cerium in the Presence of Other Rare Earths by the Action of Potassium Ferricyanide. PHILIP E. BROWNING and HOWARD E. PALMER (*Amer. J. Sci.*, 1908, [iv], 26, 83-84; *Zeitsch. anorg. Chem.*, 1908, 59, 71-73).—To a measured portion of the cerous sulphate (containing about 0.1 gram of cerium), which may contain also the sulphates of the other rare earths, are added 20 c.c. of 2% ferricyanide solution, and then a slight excess of aqueous potassium hydroxide. The precipitate is filtered off, and the filtrate and washings, amounting to about 200 c.c., are slightly acidified with dilute sulphuric acid, and the ferrocyanide formed by the reducing action of the cerous salt is then titrated as usual with standard permanganate; 2 mols. of ferrocyanide = 1 mol. of cerous oxide.

L. DE K.

Estimation of Iron and Vanadium in the Presence of Each Other. GRAHAM EDGAR (*Amer. J. Sci.*, 1908, [iv], 26, 79-82; *Zeitsch. anorg. Chem.*, 1908, 59, 74-78).—The process is based on the fact that ferric iron is reduced to the ferrous state both by the action of sulphur dioxide and amalgamated zinc, but in the case of vanadic acid, the reducing action of sulphur dioxide goes as far as V_2O_4 only, but that of zinc to V_2O_3 . The difference in permanganate used for re-oxidation after reduction with sulphur dioxide and the second reduction with zinc is a measure for the amount of vanadium present.

The solution is saturated with sulphur dioxide, a few c.c. of dilute sulphuric acid are added, and the liquid boiled in a current of carbon dioxide free from air. When all the sulphur dioxide has been removed, the flask is cooled rapidly, and the liquid titrated with standard permanganate until the colour changes from blue to yellowish-green; the liquid is then heated to 70-80°, and the titration continued. The liquid is now passed through a column of amalgamated zinc contained in a long Jones' reductor, being preceded by 150 c.c. of hot dilute 2½% sulphuric acid. After washing the zinc with 100 c.c. of the acid and then with 200 c.c. of water, the contents of the receiving flask (into which some pure ferric sulphate had been introduced, and which has been kept cool) are mixed with syrupy phosphoric acid and titrated with permanganate until the reaction is nearly at an end; the temperature is then raised to 70-80°, and the titration continued.

L. DE K.

Simultaneous Volumetric Estimation of Iron and Vanadium [in Ferro-Vanadium]. T. WARYNSKI and B. MDIVANI (*Ann. Chim. anal.*, 1908, 13, 210-212).—Three to four grams of the alloy are treated several times with nitrohydrochloric acid and nitric acid and evaporated to dryness, and the residue is boiled with dilute nitric acid and filtered

off from any silica. The filtrate is then evaporated with addition of hydrogen peroxide, and then again several times with sulphuric acid to expel the nitric acid. The mass is then dissolved in very dilute sulphuric acid, and diluted to 500 c.c.; 100 c.c. are taken for the estimation of the vanadic acid only by Bunsen and Mohr's method (distillation with hydrochloric acid, collecting the distillate in potassium iodide, and determining the iodine liberated). Another 100 c.c. are then taken for the joint estimation of the ferric oxide and vanadic acid by the authors' stannous chloride method (compare this vol., ii, 636).

L. DE K.

Estimation of Chromium as Silver Chromate. FRANK A. GOOCH and L. H. WEED (*Amer. J. Sci.*, 1908, [iv], 26, 85—86; *Zeitsch. anorg. Chem.*, 1908, 59, 87—93).—Chromium in the state of chromate or dichromate may be accurately estimated by adding to the solution an excess of silver nitrate, then a slight excess of ammonia, and finally acetic acid to slightly acid reaction. The silver chromate is collected on a Gooch filter, washed first with a dilute solution of silver nitrate to remove any soluble impurities, and then with small portions of water, 20—30 c.c. in all. The precipitate may be dried at 135°, or gently over a naked flame.

L. DE K.

Estimation of Tungstic Acid and its Separation from other Substances by means of a Mixture of Chlorine and Sulphur Chloride. FRANÇOIS BOURION (*Compt. rend.*, 1908, 146, 1102—1104).—It has been shown previously (*Abstr.*, 1904, ii, 341) that tungsten trioxide when heated strongly in a mixture of chlorine and sulphur chloride yields volatile oxychlorides, and the method now proposed is based on this reaction; it is applicable to the estimation of tungsten trioxide in sodium tungstate, silicotungstic acid, &c. A portion of the sample is placed in a porcelain or silica boat, and is then heated in a glass tube through which a current of chlorine containing a little sulphur chloride is passed. The volatile substances are collected in a receiver containing water, and, when the operation is at an end, the contents of the receiver are evaporated with nitric acid, heated to remove sulphuric acid, the residue is taken up with ammonium nitrate solution, and the tungsten trioxide is collected on a filter and weighed. If any of the oxychloride condenses on the sides of the glass tube, the latter may be rinsed with ammonia and the solution added to the contents of the receiver. The silica may be recovered by extracting the contents of the boat with water and weighing the residue.

W. P. S.

A New Method of Separation of Silica and Tungsten Trioxide. EDOUARD DEFACQZ (*Compt. rend.*, 1908, 146, 1319—1320. Compare *Abstr.*, 1907, ii, 475; Marignac, *Ann. chim. Phys.*, 1864, [iv], 3, 9; Friedheim, Henderson, and Pinagel, *Abstr.*, 1905, ii, 614; Bourion, preceding abstract).—This is based on the facts that silica is unattacked, but tungsten trioxide is reduced by hydrogen at 600—900° either to lower oxides or to the metal, and that the latter are converted by chlorine into the volatile hexachloride

or oxychlorides. The mixture of silica and tungsten trioxide contained in a boat is heated to redness in a current of hydrogen. When the reduction is complete, the boat is introduced into a glass tube bent so as to admit of the condensation of volatile products, and heated in a current of dry chlorine. If the reduction has been complete and all the air has been expelled, a mixture of tungsten hexachloride and oxytetrachloride is volatilised, otherwise the product consists of a mixture of the red and yellow oxychlorides.

The receiver is washed out with dilute ammonia, and the tungsten estimated in one of the known ways. The silica remains in the boat, and should be quite white; it should give no colour reaction when fused with potassium hydrogen sulphate.

The method is generally applicable to mixtures of two oxides, only one of which is reduced by hydrogen to a metal, forming with chlorine a volatile chloride.

E. H.

Tables for Converting Percentages of Alcohol by Volume into Percentages by Weight. A. BLONDEAU (*Bull. Assoc. chim. Sucr. Dist.*, 1908, 25, 1032—1045). The tables given show the weights of alcohol corresponding with volumes of alcohol as determined by Gay-Lussac's hydrometer in mixtures of alcohol and water containing from 1 to 100% of alcohol by volume at any temperature between 0° and 30°

W. P. S.

Estimation of Alcohol and Extract in Spirits by means of the Refractometer. JOSEPH RACE (*J. Soc. Chem. Ind.*, 1908, 27, 547—548).—A table is given showing the refractive indices of mixtures of alcohol and water containing from 1 to 100% of alcohol, the indices being given for each difference of 1%. Using this table, it is possible to estimate the quantity of alcohol and extract in a spirit. The refractive index of the spirit is taken at a temperature of 15.5°, and also that of the liquid obtained by evaporating 25 c.c. of the spirit almost to dryness and diluting the residue to the original volume. The difference between these results is due to the alcohol and other volatile constituents, and the difference between the refractive index of the extract and that of water is due to the extractive matters contained in the spirit.

W. P. S.

Messinger and Vortmann's Method of Estimating Phenols. Separation of Salicylic Acid. J. BOUGAULT (*Compt. rend.*, 1908, 146, 1403—1405).—The violet-red compound obtained by Messinger and Vortmann (*Abstr.*, 1889, 1150) by the action of iodine and potassium hydroxide on phenol, and formed in these authors' method of estimating phenol (*Abstr.*, 1890, 1473), is not a di-iododibenzene, $C_6H_3I_2O$, but a mixture of 2:4:6-tri-iodophenol with the red substance obtained by Lautemann (*Annalen*, 1861, 120, 309), and shown by Benzinger and Kämmerer (*Abstr.*, 1878, 574) to be tetraiododiphenylenequinone.

Similarly, the substance obtained by Messinger and Vortmann from salicylic acid is a mixture of the same red substance with potassium 3:5-di-iodosalicylate. The extreme insolubility of

mann's red substance furnishes a means of estimating and separating salicylic acid. For example, a mixture of 0.1 gram of salicylic acid and 0.2 gram of cinnamic acid is dissolved in 50 c.c. of water and 1 gram of sodium carbonate. Excess of iodine is added, the whole heated on the water-bath for twenty minutes, and finally boiled for ten minutes under reflux, iodine being added from time to time to ensure excess being present. The latter is removed by sodium sulphite, and the precipitate collected on a Gooch crucible. The weight multiplied by 138/344 gives the weight of salicylic acid.

Lautemann's red substance is produced by the action of iodine on a solution of 2 : 4 : 6-tri-iodophenol in sodium carbonate.

J. C. C.

Estimation of Orcinol in Orchella "Weed." HENRY EDGAR WATT (*J. Soc. Chem. Ind.*, 1908, 27, 612).—The following method of estimating orcinol in Orchella weed (the name usually given to the lichen *Rocella tinctoria*) is given. Two grams of the powdered lichen are mixed in a mortar with 2 grams of sodium carbonate, and water is then added gradually until the mixture has a volume of 100 c.c. After being stirred occasionally for twenty minutes, the mixture is poured on a filter, and 50 c.c. of the filtrate are treated with an excess of standardised sodium hypochlorite solution. An excess of $N/10$ arsenious acid solution is immediately added, and the excess is titrated back with sodium hypochlorite solution, using as indicator starch-iodide solution acidified with acetic acid. The sodium hypochlorite solution must be standardised on pure orcinol. Four samples of orchella weed from the Seychelles were found to contain 11.5%, 1.6%, 8.8%, and 9.3% of orcinol respectively. In addition to the instantaneous reaction between orcinol and sodium hypochlorite on which the above method is based, a secondary and slower reaction appears to take place, and is not completed within twenty-four hours.

W. P. S.

Estimation of Sugar. IVAR BANG (*Biochem. Zeitsch.*, 1908, 11, 538—540).—Further details of the author's method are given, and Jessen-Hansen's remarks on the theory of the reaction criticised.

W. D. H.

Detection of Dextrose in Urine. ANDREAS OTTO (*Pharm. Weekblad*, 1908, 45, 809—813).—Kowarsky's phenylhydrazine test may be recommended, but the precipitate should be recrystallised from alcohol in order to obtain the typical crystalline form of the glucosazone; a slight excess of acetic acid does not influence the result. A rapid crystallisation does not affect the nature or the size of the crystals. Two minutes boiling with the reagent is not necessary, although desirable; addition of sodium chloride is not always necessary. The reaction with alkaline bismuth solution (Nylander's test) is accelerated and rendered more delicate by adding a few drops of platonic chloride, but attempts to make this a quantitative process by measuring the volume of the precipitate utterly failed, although there is no doubt as to the complete elimination of the dextrose. The addition of

platinic chloride is particularly of service if the phosphates have not been removed previously.

The ordinary Fehling test for sugar is not influenced by platinic chloride.

L. DE K.

Detection of Sucrose. M. EMMANUEL POZZI-ESCOFF (Bull. Assoc. chim. Sucr. Dist., 1908, 25, 1078).—A portion of the solution under examination is placed in a test-tube, and about 10 c.c. of concentrated sulphuric acid are then introduced, the test-tube being inclined so that the two liquids do not mix. If sucrose is present, a coloured ring appears at the junction of the liquids; the ring is red below and yellow above. The test will detect the presence of 0.00005 gram of sucrose. The reaction is also given by other carbohydrates, but it is most sensitive in the case of sucrose.

W. P. S.

Detection of Glycuronic Acid by B. Tollens' Method in Human Urine. KARL TOLLENS (*Zeitsch. physiol. Chem.*, 1908, 53, 115—116. Compare B. Tollens, this vol., ii, 639).—To 5 c.c. of urine, 0.5 c.c. of a 1% alcoholic solution of naphtharesorcinol and 5 c.c. of hydrochloric acid (D 1.19) are added; the solution is boiled for one minute over a small flame, left for four minutes, cooled, and extracted with ether. When glycuronic acid is present, the ether is coloured intensely blue, and when examined spectroscopically, shows a band near the sodium line.

G. B.

Estimation of Tartaric Acid in Argol and Wine Lees. M. EMMANUEL POZZI-ESCOFF (*Compt. rend.*, 1908, 146, 1031—1032; *Ann. chim. anal.*, 1908, 13, 266—269; *Bull. Soc. chim. Belg.*, 1908, 22, 218—221; *Bull. Assoc. chim. Sucr. Dist.*, 1908, 25, 964—967).—The method proposed depends on the insolubility of barium tartrate in alcohol, and on the solubility of barium bromide in this medium. A weighed quantity of about 1 gram of the sample is treated with an excess of potassium carbonate solution, and the mixture is boiled and diluted to a volume of 100 c.c. Twenty-five c.c. of this solution are acidified with hydrochloric acid, boiled to remove carbon dioxide, and then rendered alkaline with ammonia. Forty c.c. of N/10 alcoholic solution of barium bromide and about 75 c.c. of 95% alcohol are added, the mixture is stirred, and the precipitate, consisting of barium tartrate, is collected on a filter and washed with alcohol. The precipitate may then be converted into barium sulphate and weighed as such, the tartrate being calculated from the weight of sulphate found, or the excess of barium bromide may be estimated in the filtrate. For this purpose, the filtrate is diluted with water, ammonium oxalate is added, the barium oxalate is collected on a filter, washed with dilute ammonia, then decomposed with hot dilute sulphuric acid, and the oxalic acid in the solution titrated with potassium permanganate solution. The difference between the quantity of barium bromide added and that found as oxalate in the filtrate is equivalent to the tartaric acid in the sample.

W. P. S.

Viscosity and Lubrication. CHARLES F. MABERY and J. HOWARD MATHEWS (*J. Amer. Chem. Soc.*, 1908, 30, 992—1001).—The viscosity of lubricating oils is usually regarded as a standard of quality, but probably does not afford a trustworthy indication of the comparative durability of oils differing widely in composition. If the viscosity constant is supplemented by chemical data and frictional durability tests, it may no doubt be depended on as giving accurate information for commercial purposes. A large number of hydrocarbons obtained by the fractional distillation of petroleum have been examined, and a series of frictional tests have been carried out with them in comparison with castor, sperm, and rape oils.

The lubricating value depends on the temperature reached during the frictional test, the degree of friction, and the time for which the oil continues to lubricate. The durability of the individual hydrocarbons increases with decrease in hydrogen, and in a similar ratio to the increase in specific viscosity. A hydrocarbon of the series C_nH_{2n-4} was found to be more efficient in reducing friction than castor, sperm, or rape oil. It was equal to sperm oil in temperature and coefficient of friction, and superior to castor and rape oils in durability.

With regard to the comparative value of the various series of hydrocarbons in petroleum from which lubricating oils are prepared, those of the C_nH_{2n+2} series have a low lubricating value. Lubricating oils from Pennsylvania petroleum consist chiefly of the C_nH_{2n} and C_nH_{2n-2} series, whilst those from the heavier oils are composed largely of hydrocarbons of the C_nH_{2n-2} and C_nH_{2n-4} series.

Comparative examination of distillates from South American and Pennsylvania petroleums has shown that neither sp. gr. nor b. p. can be depended on as indicating the lubricating value unless the source of the oil is known.

Nothing is at present known as to the constitution of the series of hydrocarbons in lubricating oils. E. G.

Analysis of Hyposulphites and their Compounds with Formaldehyde. W. F. GREAVES (*J. Soc. Dyers*, 1908, 24, 195—196).

—For the estimation of formaldehyde in the formaldehyde compound of sodium hyposulphite, the method described by Cross, in which the compound is heated with chromic acid, is recommended as being trustworthy. A Lunge's nitrometer is employed for measuring the carbon dioxide produced. The inner tube of a Lunge bottle is filled with 5 c.c. of cold saturated chromic acid solution, and 10 c.c. of a 10% solution of the compound under examination are placed in the part of the bottle surrounding the tube. The bottle is then connected with the nitrometer, the contents of the bottle are mixed and gently heated until the mixture just boils, the bottle is next cooled by placing it in cold water, and, at the end of one hour, the volume of the carbon dioxide is read off, the usual corrections for temperature, pressure, &c., being made. The method described by Knecht and Hibbert (*Abstr.*, 1907, ii, 907) for the estimation of sodium hyposulphite can be applied to the analysis of hyposulphite compounds which are not decomposed by water. W. P. S.

Folin's Method for Separating Acetone and Acetoacetic Acid in Urine. T. STUART HART (*J. Biol. Chem.*, 1908, 4, 473-476, Compare Abstr., 1907, ii, 588).—Folin's method was found to be a valuable one. In cases where acetone is excreted, the amount is far more constant than that of acetoacetic acid. If the total amount of the two substances increases, the increase is largely due to the acetoacetic acid.

W. D. H.

Separation of Ammonia and Amines by means of Boiling Absolute Alcohol. JEAN BERTHEAUME (*Compt. rend.*, 1908, 146, 1215-1217; *J. Pharm. Chim.*, 1908, 28, 8-13. Compare Jarry, Abstr., 1899, ii, 738; Brochet and Cambier, *Bull. Soc. chim.*, [iii], '13, 533).—In order to determine the trustworthiness of the method of separating amino hydrochlorides by means of boiling absolute alcohol, the author has determined the solubilities of methylamine hydrochloride, ammonium chloride, and a mixture of the two in this solvent. The amine hydrochloride was prepared from bromoacetamide, and purified from ammonia by yellow mercuric oxide.

The quantities of the salts dissolved separately were determined by evaporation of the solutions and desiccation at 110°; in the case of the mixture of the two salts, François' method of analysis (Abstr., 1907, ii, 503) was employed. The values obtained were:

100	grams	absolute	alcohol	at	82°	dissolve	23.01	grams	NH ₄ MeCl.
100	"	"	"	"	78.5	"	1.538	"	NH ₄ Cl.
100	"	"	"	"	0	"	0.773	"	NH ₄ Cl.
100	"	"	"	"	82	"	25.0	"	NH ₄ MeCl and
							2.266	"	NH ₄ Cl.
100	"	"	"	"	0	"	6.0	"	NH ₄ MeCl and
							0.65	"	NH ₄ Cl.

From these results, it is obvious that the solubility of each salt in boiling alcohol is increased in the presence of the other, that when a mixture of methylamine and ammonium hydrochlorides is extracted with boiling alcohol the two salts are dissolved in the proportion 11:1, and that on cooling to 0° the solution deposits 1.616 grams of ammonium chloride per 19 grams of methylamine hydrochloride, that is, a mixture containing 85% of the latter salt.

Employing François' method of analysis, the author finds (1) that if a saturated aqueous solution of pure methylamine hydrochloride is saturated with ammonium chloride at 15°, the product deposited on evaporation contains 9.2% of the latter salt; (2) that the crystals first deposited by a boiling alcoholic solution of Brochet and Cambier's crude methylamine hydrochloride contain 10.8% of ammonium chloride, and (3) that a saturated solution of ammonium and methylamine hydrochlorides in boiling absolute alcohol deposits, on cooling, crystals containing 8.5% of ammonium chloride.

These results are contrary to the general opinion that ammonium chloride is insoluble in saturated aqueous or alcoholic solutions of methylamine hydrochloride.

The conclusion is drawn that the method of separation is of very little use. E. H.

A Rapid and Delicate Method of Detecting Bile-pigments in Urine. WILLIAM MACADIE (*Pharm. J.*, 1908, [iv], 26, 686).—A modification of Gmelin's test. The urate precipitate, produced by adding a saturated solution of calcium chloride to the faintly acid urine, contains the bile-pigments; it is dissolved in a mixture of 1 part of hydrochloric acid (D 1.16) and 3 parts of alcohol, and while still in the centrifuge-tube, 5—6 drops of nitric acid, D 1.42, are added. G. B.

Proposed Method for the Routine Valuation of Diastase Preparations. WILLIAM A. JOHNSON (*J. Amer. Chem. Soc.*, 1908, 30, 798—805).—Commercial potato-starch is washed, pressed dry, and dried gradually finally at 80°. The remaining water, generally about 10%, is then estimated. Other starches should not be employed. A quantity corresponding with 20 grams of anhydrous starch is then stirred with 100 c.c. of water, and poured into a flask containing 800 c.c. of boiling water; the boiling is continued for ten minutes, and hot water is added up to 1000 grams.

Fifty grams of the starch solution are weighed out into a series of flasks kept at 40°. To each are added increasing portions of the diastase solution (for instance, liquid malt ten times diluted). After ten minutes each bottle is tested for free starch with dilute iodine solution. This then gives an idea of the strength of the diastase product, as it shows how much is wanted to convert the starch into dextrin and sugar in a given time. The operation is then repeated, using double the quantities of starch solution and diastase solution. As a check, the sugar formed may be estimated. L. DE K.

Colorimetric Method Applicable to both Peptic and Tryptic Enzymes. HERBERT E. ROAF (*Bio-Chem. J.*, 1908, 3, 188—192).—Grützner's method of estimating the rate of proteolysis by the amount of carmin liberated from fibrin stained with that pigment has the disadvantage that it is only applicable to enzymes which, like pepsin, act in an acid medium; if used for trypsin, the dye is liberated by the alkali employed. Congo-red may be substituted for carmin, and fibrin stained with it may be used for both peptic and tryptic ferments. W. D. H.

Ferments and Anti-ferments. VII. Detection of Trypsin. MARTIN JACOBY (*Biochem. Zeitsch.*, 1908, 10, 229—231. Compare Abstr., this vol., i, 236).—A solution of ricin or a suspension of edestin remains cloudy in the absence of trypsin, and becomes clear when trypsin is present in an alkaline medium. W. D. H.

Suchting's Method for Estimating Acidity of Soils. A. J. VAN SCHERMBECK (*J. pr. Chem.*, 1908, [ii], 77, 489—497).—In Tacke's method for estimating soil acidity (Abstr., 1908, ii, 103), it is assumed that no acid is produced during the four hours required for

the determination. It is pointed out that, whilst under natural conditions the production of acids in the soil is checked when the acidity reaches a certain limit, the soil water is greatly diluted in the process referred to, and conditions are thus produced which are favourable to increased decomposition of the organic matter; the error is further increased by addition of calcium carbonate. Süchting's modification (this vol., ii, 231) has the advantage that the time required is reduced to about half; nevertheless, it yields results which may be far too high. A peaty sand, for example, showed an amount of acid corresponding with 1.44% HCl in the soil water, which is fifty to sixty times the amount in which it is possible for roots to live.

Correct results can only be obtained under conditions of sterilisation.
N. H. J. M.

Separation of Clay in the Estimation of Humus. C. A. MOORE and H. H. HAMPTON (*J. Amer. Chem. Soc.*, 1908, 30, 805—807).—Determinations of the humus by evaporating the ammoniacal extract to dryness on a water-bath, so as to coagulate the clay, redissolving in 4% ammonia, and filtering, shows that this method gives more uniform results than direct filtration through a Pasten-Chamberland filter, which gives low results, chiefly owing to loss of humus in the filter. Peter and Averitt's method (*Kentucky Stat. Bul.*, No. 126, 63—126), in which a factor is employed for correcting for loss in the clayey residue, was also found to be unsatisfactory; the results were not concordant, and the factor (10%) too low for the soils examined.

A number of determinations of humus in soils lined three years previously, and in the unlined soils, showed that the small differences due to lime can be detected by the evaporation method described above.
N. H. J. M.

The Action of Heat on the Lecithin-Phosphoric Acid Contained in Pastry. W. LUDWIG (*Zeitsch. Nahr. Genussm.*, 1908, 15, 668—680).—It is shown that a considerable decrease in the amount of lecithin-phosphoric acid present in pastry takes place when the latter is heated for some time at a temperature of 102°. The loss is particularly marked in samples containing but little egg-material, and may amount to as much as 40%, calculated on the quantity present before the heating. The decrease is not due to loss of volatile phosphorus compounds, but to a portion of the lecithin being rendered insoluble in the solvents employed in the estimation of the lecithin-phosphoric acid. The total amount of phosphoric acid is the same after as before the heating. A small decrease in the amount of lecithin-phosphoric acid was also noticed when the pastry was kept for a few months. The author finds that practically the whole of the lecithin-phosphoric acid may be obtained in solution by boiling the pastry three times with absolute alcohol, the boiling being continued for twenty minutes each time.
W. P. S

General and Physical Chemistry.

Magnetic and Electric Double Refraction of Nitrobenzene. Variation with Wave-length. A. COTTON and HENRI MOUTON (*Compt. rend.*, 1908, 147, 193—195. Compare Abstr., 1907, ii, 727; this vol., ii, 2).—The differences between the ordinary and extraordinary indices of refraction of nitrobenzene in the magnetic field increase regularly when the wave-length of the light diminishes. Measurements have been made with the yellow, green, and indigo mercury lines, and with the *C* and *F* lines of hydrogen. Kerr's phenomenon has been studied in the case of pure nitrobenzene, using small differences of potential, and it is found that the dispersion is the same in the case of electric as in the case of magnetic double refraction; the temperature-coefficient is also approximately the same for each. The two phenomena therefore appear to have a common origin, and this may be sought in molecular orientation. W. O. W.

Spectrum of the Discharge from a Glowing Lime Cathode in Mercury Vapour. F. HORTON (*Proc. Camb. Phil. Soc.*, 1908, 14, 501—507).—The spectrum of the discharge between an electrically heated Wehnelt cathode and an aluminium anode exhibits five new lines, which are shown to be due to mercury. The wave-lengths of the lines are 6912, 6715, 6232, 6121, and 6070. The fact that these have not been described previously is supposed to be due to their absence from the ordinary arc or spark spectrum. H. M. D.

Spectra of the Calcium Flame. GUSTAVE A. HEMSALECH and CHARLES DE WATTEVILLE (*Compt. rend.*, 1908, 147, 188—190).—A spectrophotographic study of the calcium flame obtained by the apparatus previously described (this vol., ii, 336). The spectra are considerably richer in lines than the flame spectra hitherto obtained. A table is given showing the wave-lengths of the lines and also their relative intensities when the spark is used in conjunction with air-gas, air-hydrogen, oxygen-coal gas, and oxyhydrogen flames, and also when the de Watteville pulverisation method with an air-gas flame is employed. W. O. W.

Absorption Spectra of some Compounds obtained from Pyridine and Collidine. JOHN E. PURVIS (*Proc. Camb. Phil. Soc.*, 1908, 14, 435—440. Compare Baker and Baly, *Trans.*, 1907, 91, 122).—The absorption band of 3:5-dichloropyridine is found to be displaced towards the red end of the spectrum when compared with that of pyridine. The amount of the displacement and the persistence of the band are, however, smaller than has been found in the case of 2:4:5-trichloropyridine. These effects are in agreement with previous observations relating to the influence of the introduction of chlorine into the pyridine nucleus.

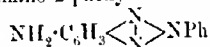
The absorption band of collidine hydrochloride is also displaced towards the red end relatively to that of the free base, and the persistence of the band is increased by union with hydrochloric acid.

Observations have also been made with the heptachlorolutidine obtained by Sell and Foster from the enneachlorocollidine previously examined. Compared with that of the latter substance, the absorption band of heptachlorolutidine is displaced towards the red, and its persistence is considerably greater.

H. M. D.

Change of the Colour of Fluorescence with the Solvent.

HEINRICH LEY and K. VON ENGELHARDT (*Ber.*, 1908, 41, 2509—2516).—It has been observed repeatedly that the colour of fluorescence depends on the nature of the solvent in which the fluorescent substance is dissolved. Kehrman and Messinger (*Abstr.*, 1892, 889) and Kauffmann and Beisswenger's investigations (*Abstr.*, 1905, ii, 131) point to a relation between the colour of fluorescence and the dielectric constant of the solvent, whilst Stark (*Abstr.*, 1907, ii, 147) draws attention to the relation of fluorescence to selective absorption. The present authors have now studied the changes in the absorption spectra of substances with varying fluorescence when dissolved in various solvents, the absorption curves being carried into the ultra-violet. As objects of study were chosen 5-amino-2-phenyl-2:1:3-benzotriazole,



(Kehrman and Messinger, *loc. cit.*), and dimethylnaphtheurhodine (Kauffmann and Beisswenger, *loc. cit.*) in methyl-alcoholic, ethyl-alcoholic, ethereal, chloroform, ethyl acetate, and carbon disulphide solutions. The results are tabulated and expressed in curves.

It is found that with the benzotriazole, the fluorescence changes from bluish-green through blue to bluish-violet, and the absorption is shifted towards the ultra-violet when the base is dissolved in alcohol, ether, and chloroform in the order named. That the solution in carbon disulphide is not fluorescent is to be ascribed to the formation of an additive compound, in agreement with which it is found that the solution in carbon disulphide is stable towards light, whereas the solutions in other solvents, especially in chloroform, are rapidly decomposed on exposure to light. The fluorescence is weakened by addition of acids, but disappears only in presence of an excess of hydrochloric acid; this change also is expressed in the absorption curve. It is probable that the hydrochloride fluoresces in the ultra-violet.

With the eurhodine base, also, the colour of the fluorescence changes with the shifting of the absorption towards the ultra-violet, but in the order of solvents: alcohol, chloroform, ethyl acetate, ether, from reddish yellow through yellowish-green to yellow.

G. Y.

Fluorescence and Photo-electric Sensitiveness of Organic Substances. JOHANNES STARK and W. STEUBING (*Physikal. Zeitsch.*, 1908, 9, 481—495. Compare *Abstr.*, 1907, ii, 147, 417; this vol., ii, 138).—The authors have made experiments on a large number of

substances to ascertain the relationship between fluorescence, on the one hand, and the nature of the banded absorption spectrum and the photo-electric effect, on the other.

Benzene and derivatives of it containing no other chromophoric group exhibit fluorescence bands which, like the corresponding absorption bands, decrease in intensity with increasing wave-length. The fluorescence spectrum of benzene is situated in the region of smallest wave-lengths, substitution of one or more hydrogen atoms leading to a displacement of the spectrum towards greater wave-lengths. The same phenomenon is met with in the case of condensed or coupled ring compounds. The displacement produced by successive substitution shows a gradual decrease. Of the various substituting groups investigated, the methyl group produces the least displacement and the amino-group the greatest. The fluorescence spectrum of benzene, naphthalene, anthracene, phenanthrene, and certain other aromatic hydrocarbons consists of several distinct bands, but if hydrogen in the ring is substituted by another element or group, or if two benzene rings are coupled by other atoms than carbon and hydrogen, a continuous spectrum is obtained. Substances containing a chromophoric group, but not a benzene ring, do not exhibit fluorescence.

As a result of the examination of the photo-electric properties, the conclusion is drawn that substances which fluoresce are also photo-electrically active. The greater the photo-electric effect the more intense is the fluorescence. Quinine sulphate is an exception, and it is suggested that this is due to a difference in the constitution of the solid and the dissolved substance.

The fluorescence of benzene derivatives containing another chromophoric group has been examined. The behaviour of these can be anticipated from that of the two simpler classes of substances.

An explanation of the phenomena of fluorescence and of photo-electric activity is given in terms of the electronic theory discussed in the authors' previous papers.

H. M. D.

A Case of Anomalous Rotatory Dispersion. Application of Measurements of Rotatory Dispersion to the Study of the Composition of Oil of Turpentine. EUGÈNE DARMOIS (*Compt. rend.*, 1908, 147, 195—197).—French levorotatory turpentine has practically constant properties, and probably contains *l*-pinene. Other oils are usually dextrorotatory, and probably contain *d*-pinene. The rotatory dispersion of certain *l*- and *d*-oils has been studied, and it is found that the dispersion is normal, but varies with the oil examined. Certain mixtures of *d*- and *l*-oils, however, exhibit anomalous dispersion, the results not being in accordance with those calculated from Biot's law of mixtures. These mixtures can, moreover, be produced by distillation of any *d*-oil, by stopping the operation at the right point. The conclusion is drawn that the two *d*- and *l*-oils are not chemically homogeneous. Crystallisable *l*-pinene has been isolated from the *l*-oil. The *d*-oil probably contains *d*-pinene together with an unknown substance having less dispersive power than *l*-pinene.

W. O. W.

Triboluminescence of Racemic Compounds. DESIRÉ GERNEZ (*Compt. rend.*, 1908, 147, 11—15. Compare Tschugaeff, *Abstr.*, 1905, ii, 132).—A number of *d*- and *l*-tartrates and the corresponding racemates have been examined with the object of testing Tschugaeff's theory, that when the two active forms are triboluminescent the racemic compound is not. In confirmation of the theory, the author finds that *l*-tartaric acid, like the dextro-modification, is triboluminescent and racemic acid is not. Dextro- and laevo-potassium tartrates and potassium racemate, and *d*- and *l*-ammonium tartrates and ammonium racemate, obey the rule, as also does the double racemate of sodium and potassium, the constituents of which are both triboluminescent. Contrary to Tschugaeff's statement, acid potassium racemate is triboluminescent as well as the acid potassium tartrates.

The following substances are all triboluminescent and contrary to Tschugaeff's theory: the normal tartrates and racemates of rubidium, sodium, and thallium; the acid tartrates and racemates of ammonium, potassium, rubidium, sodium, and thallium, and the double racemates of ammonium-lithium, antimonyl-potassium, cesium-lithium, lithium-potassium, lithium-rubidium, lithium-sodium, lithium-thallium, rubidium-sodium, sodium-thallium. Lithium racemate is triboluminescent, but the lithium tartrates could only be obtained in a non-crystalline condition, and appeared to give no light when crushed.

The *d*- and *l*-tartrates and the racemates of quinine, strychnine, and brucine, and the acid *d*- and *l*-tartrates and acid racemates of cinchonine, strychnine, and brucine, are all crystalline substances exhibiting triboluminescence.

There are only six authentic cases in favour of Tschugaeff's rule as compared with a large number in opposition to it. No general relation can be detected between molecular symmetry and triboluminescence.

R. J. C.

Thermodynamic Treatment of Photochemical Processes. FRITZ WEIGERT (*Zeitsch. physikal. Chem.*, 1908, 63, 458—466).—Various formulae are deduced by the author, and their bearing on the experimental results obtained by Luther and Weigert (*Abstr.*, 1905, ii, 785) are discussed. He reaches the result that in the system anthracene-dianthracene the energy which is chemically utilised in unit time is in all cases practically proportional to the light absorbed by the anthracene. If this is accepted, then it is possible on a thermodynamic basis alone to interpret all the experimental results observed by Luther and Weigert. The electrochemical theory recently propounded by Byk (this vol., ii, 339) appears to be unnecessary.

J. C. P.

Emission of Electricity from the Induced Activity of Radium. WILLIAM DEANE (*Amer. J. Sci.*, 1901, [iv], 26, 1—15).—The rate of decay of the induced activity of radium has been investigated by measurements of the quantity of electricity carried by the α and β rays instead of the ions produced by these. The induced

activity was deposited on the surface of a small metallic cylinder, which, during the electrical measurements, was supported co-axially inside a tube of the same metal in such a way that the distance between the outer surface of the cylinder and the inner surface of the tube only amounted to 0.44 mm. The current flow between the cylinder and the tube was measured by means of a quadrant electrometer.

The decay curves obtained in this way do not coincide with the curves corresponding with the diminution of the ionisation, and this is attributed to the emission of negative rays by radium-*B*. From the variation of the rate of discharge with the time, the conclusion is drawn that the same quantity of electricity is discharged when radium-*B* changes into radium-*C* as when radium-*C* changes into radium-*D*.

In a magnetic field parallel to the active surface, or an electrical field normal to the surface, the rate of discharge is altered; the magnitude of the observed effects is what would be expected if the charge were carried by electrons moving with velocities, normal to the active surface, of, or less than, 4×10^8 cms. per second.

The number of ions produced by the α -rays in air is less than 9000 times, and probably less than 3600 times the number of β -particles emitted by the active deposit in the same time. Assuming that each α -particle from radium-*C* produces 180,000 ions, it follows that at least 20, and probably more than 50, electrons are emitted from an active (brass) surface for every α -particle which is expelled from radium-*C*.

The experiments also show that the ionisation caused by radium-*B* and radium-*C* in the air in the immediate neighbourhood of the active surface is approximately the same.

H. M. D.

Coefficient of Absorption of Radioactive Emanations in Different Liquids. JOSÉ MUÑOZ DEL CASTILLO (*Anal. Fis. Quim.*, 1908, 6, 319—320).—A claim for priority (compare Koller, this vol., ii, 80).

W. A. D.

Photographic Impressions Produced by Radium Emanation. JOSÉ MUÑOZ DEL CASTILLO and FAUSTINO DÍAZ DE RADA (*Anal. Fis. Quim.*, 1908, 6, 322—323).—Radioactive solutions having an activity of 2,100,000 volts per hour per litre produce very good radiographs with an exposure of thirty hours; solutions with an activity of 2100 volts per hour per litre in the same circumstances do not affect the plate.

W. A. D.

Radioactivity of Swedish Spring Waters. HJALMAR SJÖGBEN and NAIMA SÄHLBOM (*Arkiv. Kem. Min. Geol.*, 1908, 3, i, No. 2, 1—28).—The authors have examined about sixty spring waters from central and southern Sweden, and find in all cases evidence of the presence of a radioactive emanation. The samples of sea-water examined were found to be inactive. The degree of activity of a spring water depends on the chemical character and quantity of the water and on the depth of the spring. In some waters the emanation

is found to be more abundant in winter than in summer. A close connexion exists between the radioactivity and geological character of a well, water from the granite showing the highest and that from sedimentary rocks the lowest activity. In all cases, the radioactivity observed was found to correspond with that of radium. The ochre deposited by some of the springs exhibits slight radioactivity, but the mud deposits are quite inactive.

T. H. P.

Radioactivity of the Waters of Lerez. JOSÉ MUÑOZ DEL CASTILLO (*Anal. Fis. Quim.*, 1908, 6, 237—242).—An investigation of the rate of decay of the radioactivity of the highly active waters of Lerez (compare Abstr., 1907, ii, 218). The initial activity probably exceeds 10,000 volts per hour per litre, and diminishes according to an exponential equation similar to that characteristic of radium; after about fifty days, however, a nearly constant residual radioactivity of about 20 volts is reached. It is probable that the radium emanation is responsible for the greater part of the radioactivity of these waters, but some other active substance is also present.

W. A. D.

Radioactivity of Waters of Agaste (Canary Islands). FAUSTINO DÍAZ DE RADA (*Anal. Fis. Quim.*, 1908, 6, 242—243).—The chalybeate water of the thermal springs of Agaste has a temperature of 25° and is decidedly radioactive, one sample having an activity of 8.9 volts per hour per litre.

W. A. D.

Radioactivity of Water from Cucho. JOSÉ MUÑOZ DEL CASTILLO (*Anal. Fis. Quim.*, 1908, 6, 350).—The water of the San Roque spring, in the valley east of Cucho, province of Burgos, contains hydrogen sulphide, and has a temperature of 15° and an initial activity of about 74 volts per hour per litre.

W. A. D.

Radioactivity of Mud from the Baths of Fitero Viejo. FAUSTINO DÍAZ DE RADA (*Anal. Fis. Quim.*, 1908, 6, 344—350).—From the character of the radioactivity of the mud, it is concluded that radium is present partly in a form soluble in hydrochloric acid and partly in an insoluble form. Thorium is entirely absent, but actinium may be present.

W. A. D.

Radioactivity of Potassium and other Alkali Metals. J. C. McLENNAN and W. T. KENNEDY (*Physikal. Zeitsch.*, 1908, 9, 510—512.* Compare Abstr., 1907, ii, 217, 597).—The radioactivity of a large number of potassium salts and of certain salts of sodium, ammonium, lithium, rubidium, and calcium has been examined by measuring the saturation current produced by the various salts when distributed in thin uniform layers on the base of an ionisation chamber. All the potassium salts and metallic potassium were found to be radioactive, but when the activities are divided by the percentages of potassium in the various compounds, numbers are obtained which vary in the ratio of one to thirty-three. The author considers that this precludes the possibility that the radioactivity is a normal property of the potassium atom. With the exception of one

* and *Phil. Mag.*, 1908, [vi], 16, 377—395.

sample of rock salt out of three examined, all the sodium salts and metallic sodium were found to be inactive. Ammonium chloride was found to be slightly active, rubidium alum and cesium chloride still less so, and the other salts showed no trace of activity. The activity of the salts other than those of the alkali metals is supposed to be due to traces of radioactive impurities.

The activity of the potassium salts is unchanged on heating, and attempts to separate active impurities by electrolysis, recrystallisation, solution in ethyl ether, and by precipitation with ammonium carbonate gave no positive result.

H. M. D.

Nature of the γ -Rays. JOSEPH J. THOMSON (*Proc. Camb. Phil. Soc.*, 1908, 14, 540).—Of the two views which have been advanced as to the nature of γ -rays: (1) that they are pulses of electromagnetic disturbance propagated through the ether; (2) that they are electrical doublets travelling with great velocity and possessing energy and momentum, it is pointed out that these approximate closely if it is supposed that the electromagnetic disturbance is distributed, not uniformly, but in patches over the wave-front. According to the pulse theory, the velocity of propagation of the rays should be equal to that of light, which is the case according to available experimental data. Barkla's measurements of the polarisation of the secondary rays produced by the γ -rays are also in accord with the pulse theory. By means of these two factors, it is possible to differentiate between the two theories.

H. M. D.

Velocity of Secondary Cathode Rays from Gases. JOSEPH J. THOMSON (*Proc. Camb. Phil. Soc.*, 1908, 14, 541—545).—The blue pencil of cathode rays emanating from a Wehnelt cathode, on which the line is confined to a small area, is surrounded by a blue haze. This is due to secondary rays produced by impact of the primary cathode rays against the gas molecules. If a piece of metal is inserted in the region occupied by the haze and the metal is negatively charged to a moderate potential, the negative particles of the haze are repelled and the metal is surrounded by a well-defined dark space. Experiments are described the object of which was to determine the difference of potential required to stop the negative particles. It is found that this potential difference is independent of the potential of the primary discharge, indicating that the energy of the secondary rays is independent of that of the primary rays. This result is in agreement with the view that the energy in the secondary rays is determined by the atoms emitting them. The energy of the secondary rays does not seem to vary much with the nature of the atoms emitting them, for air, hydrogen, and carbon dioxide give the same value, and this is very nearly equal to the value found by Füchtbauer for the secondary rays from metals.

From the potential difference required to stop the secondary rays, the velocity of these is calculated to be 3.7×10^8 cms. per second.

H. M. D.

Positive Electrons. JEAN BECQUEREL (*Compt. rend.*, 1908, 147, 121—124. Compare *Abstr.*, 1907, ii, 421).—In order to justify the

suggestion that several experiments are best explained by assuming the existence of free positive electrons, the author critically examines his results to see whether they are explainable on any other hypothesis.

In the modified Crookes tube previously described, the beam issuing through the hole in the principal cathode appears to be separated by a magnetic field into (1) strongly deviated cathode rays (negative electrons); (2) canal rays (positive ions), which, being presumably attracted by the cathode corpuscles, are slightly deviated in the same direction; (3) rays which are strongly deviated in the opposite direction. The last are supposed to consist of positive electrons.

The positive charges direct themselves towards a second cathode, which is ring-shaped, and having passed through, produce a phosphorescence on a disk of willemite, although they are no longer deviable by a magnetic field. This phosphorescence is not due to the canal rays, which have insufficient penetrating power to reach the willemite. If the willemite disk is brought near to the second cathode, a phosphorescent patch due to canal rays can be seen distinct from that due to positive electrons. The former patch is practically unaffected on bringing a magnet near the second cathode, whereas the latter is notably displaced. The phosphorescent spot due to positive electrons is in respect of position, intensity, and shape independent of the distance of the willemite from the second cathode. The spot due to canal rays, on the other hand, is scarcely perceptible unless the willemite is quite near the second cathode and is negatively charged. Alteration of the electric field by bringing the hand near the tube is sufficient to displace the canal rays, whilst the beam of positive electrons, being apparently not electrified, remains unaffected.

The positive deviable beam cannot consist of ions, because these would be attracted by the cathode stream in the opposite direction to that which the beam in question actually takes. The attraction would, however, be small, and as a matter of fact the canal rays are but slightly deviated along with the cathode stream.

The two images formed on the willemite are not due to canal rays going partly through the ring cathode and partly round it. In one vacuum tube in which this was possible, the canal rays produced a phosphorescent image of the ring cathode on the willemite, but the other, a strong phosphorescent spot, was always present as well.

The deviable ray cannot consist of positive ions of low velocity, since positive ions travelling with the same *E.M.F.* (the canal ions) are already present, and are hardly deviable. The fact that the beam in question, after passing through the second cathode, is apparently no longer electrified, suggests that it is a combination of positive ions with negative electrons. Righi, however, has shown (*Atti R. Acad. Lincei*, 1908, 17, 87) that such systems would, in a magnetic field, be deviated parallel to the lines of force.

Having failed to explain the phenomena by any recognised form of radiation, the author was led to consider the deviable rays as positive electrons liberated by the action of cathode rays on canal rays. The mechanism by which positive electrons are liberated is still obscure.

Perhaps they are grouped at the centres of atoms, and are attracted out by the atmosphere of cathode corpuscles. The negative electrons may act like projectiles against the positive ions which constitute canal rays.

The rapidity with which positive electrons disappear when they emerge from the atmosphere of negative electrons is surprising. The beam beyond the second cathode must be a flux of neutral material formed when the positive electrons disappear. The positive electrons may then have re-combined with the gas in the tube, but if the isolation of two kinds of electrons can be supposed to constitute the complete disintegration of matter, a bolder hypothesis is permissible, namely, that positive electrons combine directly with negative electrons, giving rise, perhaps, to hydrogen, which always appears in a Crookes tube.

R. J. C.

Ionised Gases. A. BLANC (*Compt. rend.*, 1908, 147, 39—42).—The mobilities of positive and negative ions in mixtures of carbon dioxide with hydrogen or air in varying proportions have been measured by a modification of Rutherford's alternating magnetic field method. It is found that the curves representing the inverse of the mobility in terms of the partial pressure of one of the gases in the mixture are in all cases straight lines. An equation is deduced theoretically connecting the mass of an ion with its mobility and the molecular composition of the mixed gases. From this it follows that if the effect of collisions between ions and molecules can be neglected, the mass of an ion must be of the same order as the mass of a molecule.

A positive or negative ion produced in carbon dioxide and travelling into air assumes the ordinary velocity of air.

The author supposes that an ion consists of a cluster of molecules which are constantly interchanged with the molecules of the surrounding gas. A carbon dioxide ion entering air, speedily becomes transformed into an air ion.

R. J. C.

Bose's Phenomenon and the Laws of Contact Electrification. EDOUARD GUILLAUME (*Compt. rend.*, 1908, 147, 53—55. Compare Bose, *J. Physique*, 1902, iv, 1, 481).—The production of an *E.M.F.* when a metallic thread immersed in an electrolyte is sharply twisted and the appearance of fatigue in this phenomenon have been further investigated.

If the wire is perfectly clean and the electrolyte is without action on it, no *E.M.F.* can be obtained by twisting the metal. Metals like copper and zinc when immersed in the electrolyte become covered with a thin, grey film. In such cases, twisting the wire produces a potential difference which is independent of the direction, but proportional to the angle of torsion. A number of twists at short intervals produce a gradually diminishing electrification. If a metal which is not superficially attacked by the liquid is covered with a thin, porous film, the same effects can be produced. Thus silver may be coated with its iodide, and platinum with gelatin or a burnt on film of kaplin.

The phenomena can be explained by Perrin's rules of contact electrification (see following abstract), which enable the relative effects of various electrolytes to be calculated with considerable accuracy.

R. J. C.

The Bose-Guillaume Phenomenon and Contact Electrification. JEAN PERAIN (*Compt. rend.*, 1908, 147, 55—56).—The following explanation is given of the phenomena observed by Bose and by Guillaume (preceding abstract). When a wire covered with a thin, porous film is immersed in an electrolyte, the spongy sheath is electrified by contact along the whole of its enormous surface. The impregnating solution therefore contains an excess of ions of the opposite sign. When the wire is sharply twisted, the sheath is stretched, and a minute amount of the charged impregnating liquid is squeezed out into the external solution, leaving behind an excess of electricity of the opposite sign, which gives rise to a momentary *E.M.F.*

The extent and sign of the potential difference is determined by the nature of the contact electrification between the material of the film and the electrolyte. H^+ and OH^- ions produce strong positive and negative effects, but are paralysed by multivalent ions of opposite sign.

Electrification by torsion is analogous with electrification by filtration through a porous diaphragm.

R. J. C.

Conduction of Electricity by Metals and Amalgams. JESŮ KINSKY (*Zeitsch. Elektrochem.*, 1908, 14, 406—410).—The experiments were intended to test the question whether positively-charged ions take any part in the transport of electricity through metals. Several copper and zinc cylinders with accurately-ground surfaces of contact were placed in contact and 5200 ampere hours passed through them, but no change in weight could be detected; iron and brass gave the same result. With silver and copper plates, no change of weight occurred, and the silver was quite free from copper both before and after the experiment. A large quantity of electricity was also passed through a tube containing homogeneous barium amalgam; after the experiment, the barium was found to be still quite evenly distributed throughout the tube. It appears, therefore, that positive ions take no part in the conduction of the current.

T. E.

Relation between Current and Potential Difference in Solutions of Iodine in Potassium Iodide. Experiments with Bright Platinum Electrodes. ERICH BRUNNER (*Zeitsch. physikal. Chem.*, 1908, 63, 487—506. Compare Abstr., 1907, ii, 223).—The experiments have been carried out in the same way as previously described (*loc. cit.*). Except in the neighbourhood of the cathodic limiting current, the values obtained for the polarisation are, as a rule, only a few millivolts greater than those observed at platinised electrodes. The results obtained at the unplatinised electrodes may be expressed by the formula $\epsilon = \epsilon_0 + I(\omega_0 + q \cdot \omega')$ (compare *loc. cit.*), where q varies between 1 and 8, mostly between 2 and 5; during one experi-

ment, and generally also during a series of experiments made successively in different solutions, q is fairly constant.

It is possible that the excess of the polarisation observed at unplatinised electrodes over that found at platinised electrodes is due to a surface resistance caused by cathodic polarisation, a resistance which vanishes as rapidly as it is produced. The excess, as far as can be seen, has nothing to do with chemical polarisation. J. C. P.

Thermodynamic Calculation of Electromotive Forces. FRANZ HALLA (*Zeitsch. Elektrochem.*, 1908, 14, 411—414).—Nernst's theory of the relation between heat development and maximum work in reactions in condensed systems (Abstr., 1907, ii, 153) is tested for the case of the two reactions $2\text{Ag} + \text{PbCl}_2 = \text{Pb} + 2\text{AgCl}$ and $2\text{Ag} + \text{Hg}_2\text{Cl}_2 = 2\text{Hg} + 2\text{AgCl}$, using existing data. Satisfactory agreement is found between the requirements of the theory and the facts. T. E.

Discharge Potentials of the Ions in Solutions of Alkali Alkylloxides. GIACOMO CARRARA and ALDO BRINGHENTI (*Gazzetta*, 1908, 38, i, 698—708).—The anode potential curves of solutions of sodium methoxide in methyl alcohol and sodium ethoxide in ethyl alcohol exhibit characteristic points at 0.32—0.34 volt, referred to the potential of the decinormal calomel electrode as zero. These values, which differ so little in the two cases that they cannot be differentiated, represent the discharge potentials of the ions (OMe) and (OEt). Similar close agreement exists between the heats of formation of the corresponding sodium salts, and it is probable that the tensions of electrolytic decomposition of these salts are also nearly equal in value. Another less sharply marked point is shown by the anode potential curves between 0.60 and 0.65 volt; it is possible that this corresponds with the discharge potential of anions of small quantities of aldehydes or acids formed by the oxidising action of the platinised platinum in presence of air. The corresponding cathode potential curves exhibit a common characteristic point at 1.22 volts, which represents that of the sodium ion. T. H. P.

Stability of the Alternating Arc; a Function of the Atomic Weight of the Metallic Electrodes. CHARLES E. GUYE and A. BRON (*Compt. rend.*, 1908, 147, 49—51).—It was shown in a recent paper (this vol., ii, 561) that the minimum potential required for a stable alternating arc largely depends on the period of extinction of the arc. This theory is now applied to elucidate the results of the authors' earlier researches on short metallic arcs.

Given the same current density, gap between electrodes, period of alternation, and air pressure, the voltage required to establish a stable arc increases regularly with the atomic weight of the electrodes. For example, with arcs 5 mm. long and current density 0.04 ampere per sq. centimetre of electrode, the voltages required are: carbon, 640; magnesium, 700; iron, 850; nickel, 850; copper, 870; silver, 900; cadmium, 725; platinum, 1000; gold, 1070. Cadmium is an exceptional case, as metallic vapour is largely produced, and the arc therefore requires an abnormally low voltage.

The period of alternation being 50, the arc is extinguished and re-lighted 100 times every second. The voltage required to re-light the arc must be the greater the more rapidly the electrodes cool at each extinction. The authors suppose that the cooling of the electrodes is for the most part the result of radiation, which is almost independent of the nature of the metal. Hence, as the specific heat is inversely as the atomic weight (Dulong and Petit), the higher the atomic weight the smaller the heat content of the electrodes, the quicker the cooling, and the higher the voltage required to re-light the arc.

It may also happen that electrons projected from the incandescent cathode have a velocity which is higher the higher the atomic weight. The two explanations are not mutually exclusive.

R. J. C.

Chemical Reactions in a Magnetic Field. G. BERNST (*Physikal. Zeitsch.*, 1908, 9, 512—519).—The influence of a magnetic field on the heat development which accompanies the solution of iron in hydrochloric and sulphuric acids has been examined. The apparatus employed consisted of an electromagnet with square pole-pieces, between which a magnetic field of intensity equal to 3000 Gauss could be established. Two silvered Dewar vessels, packed in cotton-wool, were placed between the pole-pieces, and by means of a nickel-copper thermo-element the difference of temperature between the contents of the two vessels was read off at frequent intervals. One Dewar vessel served for the solution process, and the other acted as a blank to eliminate, as far as possible, temperature changes not due to the passage of iron into solution.

The estimated accuracy of the measurement of the difference between the heat of solution with and without a magnetic field is 1%, and to this extent the experimental data lead to the conclusion that a magnetic field has no influence on the amount of heat developed by the solution of iron in hydrochloric or sulphuric acids. It is shown that the differences previously obtained by Nicholls (*Abstr.*, 1886, 668) are due to secondary disturbances, and that, although it has been shown by Duhem that the development of heat in a magnetic field should theoretically be less than without a field, the difference in question is too small to be experimentally measured.

One difference between the two processes is that the rate of solution in a magnetic field is smaller, and this is attributed to the fact that the iron particles do not respond so readily to the mechanical disturbances resulting from the evolution of gas. The protection of the iron from the action of the acid by the chloride formed may also contribute to the slower rate of solution in the magnetic field.

Experiments with zinc show that the heat change and the rate of solution are not influenced by a magnetic field.

H. M. D.

Relation between Magnetic and Chemical Properties of Complex Ferric Salts. P. PASCAL (*Compt. rend.*, 1908, 147, 56—58).—The magnetic susceptibilities of a number of solutions of ferric compounds containing the same weight of iron per litre have been determined by the well-known U-tube method. It is found that as the condition of the iron is more and more removed from

the ordinary (precipitable) ferric state, the solutions become more and more diamagnetic. The gradual addition of acid to ammoniacal ferric pyrophosphate is accompanied by a corresponding increase in paramagnetism, even before the solution has attained to the ordinary ferric colour. Excess of alkali, on the other hand, accentuates the diamagnetism of a ferripyrophosphate.

Ferrimetaphosphates and ferripyrophosphates exhibit the phenomenon of magnetic double refraction.

R. J. C.

Orientation of Crystals by the Magnetic Field. Importance of Optical Properties of Mixed Liquids from the Point of View of Crystalline Symmetry. A. COTTON and HENRI MOUTON (*Compt. rend.*, 1908, 147, 51–53. Compare Abstr., 1906, ii, 146; 1907, ii, 727).—The magnetic susceptibility of a crystal in various directions may be represented by an ellipsoid. Electrical and optical properties are also represented by ellipsoids. Although the relation between the ellipsoids cannot be generally stated, the elements of symmetry of the crystal belong to all three. Crystalline fragments suspended in a liquid in a magnetic field will tend to set themselves with the long axis of their magnetic ellipsoid parallel to the lines of force. In an electric field, the long axis of the electric ellipsoid will set itself parallel to the lines of force. Crystals fall into two groups, according as the long axes of their magnetic and electric ellipsoids coincide or not. If, as in the case of the uniaxial system, the two long axes do not coincide, suspended crystals will be completely oriented by the application of electric and magnetic fields at right angles, and the liquid with its suspended crystals will be isotropic in the direction of one of the fields. Some information concerning the crystallographic properties of microscopic crystals can thus be obtained.

The author combats the conclusion of Meslin (*Compt. rend.*, 1908, 146, 1305) that the orientation of a suspended crystal by a magnetic field can alter with variation in the permeability of the suspending liquid.

R. J. C.

Glass Thermostats for Higher Temperatures. H. W. FISCHER and O. BOBERTAG (*Zeitsch. Elektrochem.*, 1908, 14, 375–376).—For temperatures above 100°, a large glass beaker containing 10 litres of paraffin oil is used; this is heated by a "cryptol" resistance enclosed in a glass tube. For temperatures below 100°, a glass vessel full of water is used; a stream of hot water, from a reservoir at constant head, flows into the vessel through a copper spiral heated by a gas flame, which is regulated by an ordinary regulator.

T. E.

Density and Latent Heat of Fusion of Ice, and the Molecular Depression of the Freezing Point in Aqueous Solutions. W. A. ROTH (*Zeitsch. physikal. Chem.*, 1908, 63, 441–446).—A critical review of the determinations of these constants recorded by various workers. The author considers the following to be the most probable values: for the density of ice at 0°, 0.9168; for the latent heat of fusion, 79.67 cal., the calorie being defined as the heat necessary to raise 1 gram of water from 15° to 16°; for the molecular depression of the freezing point, 1.858°.

J. C. P.

Solidification Phenomena Exhibited by Inorganic Salts and Salt Mixtures. WILHELM PLATO (*Zeitsch. physikal. Chem.*, 1908, 83, 447—457. Compare Abstr., 1906, ii, 521; 1907, ii, 239).—Further observations are recorded bearing on the author's method of calculating the latent heat of fusion from the special form of cooling curve described previously (*loc. cit.*). It appears that the formulae based on the earlier results may be simplified. It is shown, also, that the latent heat of fusion may be deduced from the area enclosed by (1) the actual cooling curve, and (2) the curve that would be traced if no solidification took place.

J. C. P.

Specific Heat of Barytes, Witherite, and Fused Lime. LATSCHENKO (*Compt. rend.*, 1908, 147, 58—61).—The amounts of heat required to raise 3 to 7 grams of these substances from the room temperature to upwards of 1050° have been determined by the calorimetric method.

The specific heat of barytes increases regularly from 0.114 at 150° to 0.129 at 500°, remaining practically constant at higher temperatures.

Witherite undergoes a molecular transformation at about 800°, accompanied by a sudden increase of 19 calories per gram in the total heat of warming and a noteworthy change in the specific heat.

Values obtained with fused lime point to the existence of a molecular transformation at 405—410°, accompanied by an absorption of 5 calories per gram. Lime fused in the electric furnace gives good results only on the first occasion that it is plunged into the calorimeter water, as successive wettings and heatings break up the surface. Consistent results were obtained by the use of petroleum in the calorimeter.

R. J. C.

Thermochemical Evidence for von Baeyer's Strain Theory. H. STANLEY REDGROVE (*Chem. News*, 1908, 98, 25—27).—A theoretical paper on the thermal behaviour of the hydrocarbons, molecular heats of combustion of which have been determined by Thomsen and Strohmann, considered in the light of Baeyer's strain theory. Values for the thermal equivalent of double and treble linkings are deduced, and the thermal equivalent of strains in polymethylene compounds is found to be proportional to the angle of deviation of the carbon atoms. From thermal data, the conclusion is drawn that the molecular heat of formation found for ethylene oxide and that deduced are quite in accord with the strain theory; the heat equivalent of the molecular strain in this compound is given as 18.0 cal.

J. V. E.

Explanation of the Viscosity Curve for Mixtures of Glycerol and Water. JOSÉ R. CARRACIDO (*Anal. Fis. Quím.*, 1908, 6, 320—321).—The viscosity curve obtained by plotting the values given by Martinez-Strong (this vol. i, 307) shows a critical point between the concentrations 60% and 70% of glycerol, beyond which the viscosity increases very rapidly. Examined with the ultra-microscope, solutions containing less than 50% of glycerol do not show luminous points, and present the appearance of true

solutions; solutions containing from 50% to 80% of glycerol show an increasing number of such points, and probably consist of a mixture of a true solution with colloidal glycerol in a state of pseudo-solution. Mixtures containing 90—100% of glycerol do not show points of light, and probably consist of liquid hydrogels which are completely homogeneous.

W. A. D.

Osmotic Pressure of Dextrose Solutions at 10°. HARMON N. MORSE and W. W. HOLLAND (*Amer. Chem. J.*, 1908, 40, 1—18. Compare this vol., ii, 671).—At 10°, the osmotic pressures of dextrose solutions are proportional to the concentrations, the maximum, minimum, and mean molecular pressures obtained for individual concentrations being 23·87, 23·70, and 23·80 atmospheres respectively. The excess of osmotic over gas pressure observed in the neighbourhood of 0° (*loc. cit.*) does not disappear at 10°, at which temperature the mean molecular gas pressure is 23·09 atmospheres. The mean value of the ratio of osmotic to gas pressure for 0·1N to 1·0N dextrose solutions at 10° is 1·031, the limiting values of the ratio being 1·035 and 1·027. The closer approximation of osmotic to gas pressure at 10° than at 0° is due more to the increase in gas pressure between these temperatures than to augmentation of osmotic pressure, the mean increases in molecular gas and osmotic pressures being 0·81 and 0·35 atmosphere respectively.

The following table summarises the results obtained up to the present time:

Temperature.	Mean ratio of osmotic to gas pressure.	Mean molecular osmotic pressure.
21·7—26·9°	0·993	24·01 atmo ^s .
10·0	1·031	23·80 "
0	1·052	23·45 "

T. H. P.

Explosive Crystallisation. FRANK E. WESTON (*Chem. News*, 1908, 98, 27).—The author finds that when an aqueous solution of the compound formed by the combination of a sulphite with a thiosulphate is evaporated in a partial vacuum, a stage of concentration is reached when crystallisation may be accompanied by explosive violence. It seems probable in the case of the evaporation of some sulphites that crystallisation is suddenly induced on the surface with a consequent sudden increase in the vapour pressure of the surrounding liquid, which under the very low pressure existing causes the liquid to boil violently.

J. V. E.

Theory of Dyeing. HUGO FISCHER (*Zeitsch. physikal. Chem.*, 1908, 63, 480—486).—In criticising Freundlich and Losev's theory of adsorption (*Abstr.*, 1907, ii, 534), the author argues against assuming the existence of internal surfaces in colloids. He maintains that the swelling of colloidal substances cannot be explained by reference to any sort of structure. The phenomena of swelling and of dye absorption alike are, in the opinion of the author, essentially solution phenomena. Experiments are quoted which support this view.

J. C. P.

Influence of the Medium on Brownian Motions. VICTOR HENRI (*Compt. rend.*, 1908, 147, 62—65).—Rubber latex is coagulated to a network of fine threads by addition of acids, but is agglutinated by alkalis to a mass of irregular granules without definite structure. Before coagulation sets in, the Brownian motion of the particles in the emulsion is retarded.

The author has made cinematographic photomicrographs of rubber latex diluted to 1 in 500 with water in presence of quantities of hydrochloric acid, acetic acid, sodium carbonate, carbamide, and alcohol too small to bring about coagulation. With alkali, the Brownian movements are twice as slow, and with acid nine times as slow, as in distilled water. Thus the average displacement of a particle in 1.29 second was 0.62μ in water, 0.31μ in $N/10$ sodium carbonate, and 0.07μ in $N/32$ hydrochloric acid. $N/1000$ acetic acid produced the same effect as $N/32$ hydrochloric acid, although the former is a weaker coagulating agent.

The action cannot be attributed to the electrical influence of the ions, because alcohol produces an effect which is as intense as that of acid. On the other hand, carbamide, which does not coagulate the latex, also produces no change in the Brownian movement.

Measurements show that the granules absorb alkali somewhat, and acid very strongly. The author supposes that an adsorption zone containing molecules of the coagulating agent is formed round each granule, and that this surface combination is the cause of the slackening in the Brownian motion of the granules. R. J. C.

Osmotic Pressure and Brownian Motion. JACQUES DUCLUX (*Compt. rend.*, 1908, 147, 131—134).—Colloidal solutions and very fine suspensions have been shown to possess an osmotic pressure. This has been explained on kinetic grounds, but the osmotic pressures calculated on the kinetic theory are systematically smaller than the experimental values, although of the same order. The recent work of Perrin (*Compt. rend.*, 1908, 146, 967), which leads to an almost absolute agreement between experiment and the kinetic hypothesis, is criticised. The material employed by Perrin (namely, gamboge) is not entirely insoluble, so that in the emulsions which he prepared probably some 23% of the material was in solution. Furthermore, the insoluble particles were not conclusively shown to be of uniform size, and the method of enumerating them was questionable. Thus the kinetic theory does not explain the whole of the osmotic pressures. It is also inferior to the electrification theory of colloidal solutions in explaining many other properties, particularly coagulation.

The author supposes that the osmotic pressure of a colloidal solution is the same as that of an ordinary electrolytic solution containing the same number of electrons in the condition of free ions. It must be assumed that an ion exercises the same osmotic pressure whether free or as part of the layer on an electrified granule.

The charge can be recognised by the conductivity of the granules, that is, the difference in conductivity before and after filtering the colloidal solution through collodion. Knowing the velocity of the granules, their charge, the number of ions surrounding them and the corresponding osmotic pressures can be calculated.

The author has experimented with a true colloid, ferric hydroxide, and results calculated for osmotic pressure from the conductivity are of the same order, but somewhat smaller than the experimental values. The electrical theory gives results which are quite as good as those given by the kinetic theory, and is based on experiments made with a true colloidal solution instead of with a mere suspension, the properties of which in spite of several analogies are not the same. There is nothing incompatible in the two methods of treatment, however, if the kinetic theory is correctly regarded.

R. J. C.

Ammonia Equilibrium. F. Jost (*Zeitsch. Elektrochem.*, 1908, 14, 373—375).—The author points out that the discrepancy between his measurements and those of Haber and Le Rossignol (this vol., ii, 362) is not very great at the lower temperatures. Up to 800° a difference of less than 40° in the measurement of temperature would account for it. The possible error of his own measurements is estimated at about 20°. At higher temperatures, the differences are larger, and it is suggested that in Haber's measurements the equilibrium may have been displaced towards the cooler part of the quartz tube.

T. E.

Experimental and Thermodynamic Researches on Neutral Salt Action. BORDAN VON SZYSZKOWSKI (*Zeitsch. physikal. Chem.*, 1908, 63, 421—440. Compare Abstr., 1907, ii, 238).—When carbon dioxide is passed through water containing ultramarine in suspension, hydrogen sulphide is liberated. The presence of neutral salts hinders this reaction, and there appears to be for each salt a concentration which is just sufficient to prevent any discoverable liberation of hydrogen sulphide. The author has determined these limiting concentrations in a number of cases, and regards the reciprocal of this concentration as a measure of the neutral salt action. It is found in this way that sodium salts exert a much stronger neutral salt action than potassium salts. When sodium salts alone are considered, it appears that the neutral salt action increases with the combining weight of the anion; this rule does not apply in the case of the potassium salts. As regards the comparative neutral salt action of sodium chloride and nitrate and potassium chloride and nitrate, the results of this investigation are in harmony with the author's earlier work (*loc. cit.*). There appears to be no immediate connexion between neutral salt action and the influence of the salts on gas solubility. A few experiments made with alcohol show that the general character of neutral salt action is manifest also in alcoholic solutions.

As a practical result of his work, the author advocates a method of testing the quality of a specimen of ultramarine. A sample of the best quality, suspended in a 1.4*N* solution of sodium chloride and exposed to a fairly strong current of carbon dioxide, should not liberate any hydrogen sulphide.

The influence of a neutral salt, such as sodium chloride, on the behaviour of a weak electrolyte, such as carbonic acid, is discussed in general terms on a thermodynamic basis.

J. C. P.

Velocity of the Reaction between Bromine and Benzaldehyde. WALTER HERZ and HERMANN DICK (*Ber.*, 1908, 41, 2645—2648).—In connexion with experiments on the velocity of the addition of bromine to unsaturated substances in various solvents, the reaction $2\text{PhCHO} + \text{Br}_2 = \text{PhCO}_2\text{CHPhBr} + \text{HBr}$ has been examined in chloroform, carbon disulphide, and carbon tetrachloride. The value of K , calculated for a bimolecular reaction, is almost the same and independent of the concentration in the first two solvents, but is about one thousand times as great in carbon tetrachloride.

C. S.

Inorganic Chemistry.

Hydrogen Persulphide. RUDOLF SCHENCK and V. FALCKE (*Ber.*, 1908, 41, 2600—2603. Compare Bloch and Hohn, this vol., ii, 579, 580).—The authors have obtained the trisulphide H_2S_3 by distilling the crude polysulphide under diminished pressure. It is essential to blow steam through the glass vessels, and also to boil them in sulphuric acid, in order to remove the alkali from the surface, otherwise the polysulphide decomposes during distillation. It is a colourless, strongly refracting liquid, b. p. $43-50^\circ/4.5$ mm., D_4^{20} 1.496, and n_D over 1.70. Its odour resembles that of camphor, and of the product formed by the slow combustion of sulphur. The substance is extremely volatile, and dissolves in most organic solvents, but these solutions are unstable, with the exception of that in bromoform. Analyses and molecular weight determinations agree with the formula H_2S_3 .

J. J. S.

The Polyiodide Molecule. PRO LAMI (*Boll. chim. farm.*, 1908, 47, 435—441).—A theoretical paper. From the solubility of iodine in potassium iodide solutions of various strengths, and from the electrical conductivity of potassium iodide solutions, it is deduced that undissociated potassium polyiodide has the composition KI_{12} and that it dissociates into the ions K and I^- .

No reference is made to the work of Jakowkin (*Abstr.*, 1894, ii, 271; 1896, ii, 514; compare also Dawson, *Trans.*, 1908, 93, 1308).

G. B.

So-called Crystalline Boron. HEINRICH BILTZ (*Ber.*, 1908, 41, 2634—2645).—Crystalline silicon can be obtained by Kühne's method (*D.R.-P.* 147871), but the directions for the preparation of crystalline boron do not give successful results. The author uses the following method. An intimate mixture of boron trioxide (50 grams), sulphur (75 grams), and aluminium (100 grams), or magnesium powder, is fired by a piece of magnesium ribbon. After the reaction, the fused mass is decomposed by water, the globules of aluminium separated, and

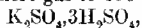
treated with hydrochloric acid. The residual black, crystalline powder is treated successively with concentrated hydrochloric acid, hydrofluoric acid, and dilute hydrochloric acid for many days. When larger quantities of materials are to be used, the proportions must be altered, more aluminium and less sulphur being taken; the yield is smaller and the black crystals are not so large. The preparation is practically an individual substance, has D_4^{20} 2.554 ± 0.005 (by the floating method), and consists of monoclinic crystals [$a:b:c = 0.7130:1:0.7139$]. A complete analysis of the substance proves it to be *aluminium boride*, AlB_{12} (compare Hampe, this Journ., 1877, i, 273). It is identical with the black modification of crystalline boron obtained by Wöhler and Deville (*Annalen*, 1858, 105, 68), the specimens of which, however, contained carbon as an impurity. The yellow, transparent crystals mentioned by these investigators have also been obtained by the preceding aluminothermic method, and will be discussed later. C. S.

Constitution of the Carbon Molecule. JOHN C. THOMLINSON (*Chem. News*, 1908, 98, 37—38. Compare *ibid.*, 1906, 93, 37).—A reply to the criticism (this vol., ii, 177) of Dewar's suggested formula for the constitution of the carbon molecule (*Chem. News*, 1908, 97, 19). J. V. E.

Presence of Rare Gases in the Atmosphere at Different Heights. L. TEISSERENC DE BORT (*Compt. rend.*, 1908, 147, 219—221).—Samples collected at Trappes from the upper regions of the atmosphere have been examined spectroscopically after removal of oxygen, nitrogen, and argon. The latter gas occurred in notable proportions. The samples collected up to a height of 10 kilometres contained both helium and neon, but helium was not detected in a sample obtained at 14 kilometres. W. O. W.

Acid Sulphates of Potassium. L. ARZALIER (*Compt. rend.*, 1908, 147, 129—131).—On evaporation of a dilute solution containing molecular proportions of sulphuric acid and potassium sulphate, there are formed various acid salts, as described by Marignac, and also crystals of the composition $4K_2SO_4 \cdot 3H_2SO_4 \cdot H_2O$, which, however, from their heat of solution do not appear to be a definite compound.

From concentrated sulphuric acid and normal potassium sulphate, the salts $K_2SO_4 \cdot 3H_2SO_4 \cdot H_2O$ and $K_2SO_4 \cdot 3H_2SO_4 \cdot 3H_2O$ were prepared, which, when heated in an inert gas to 150° , yield the salt,



previously obtained by Schultz in an impure state.

G. B.

Thioantimonates of Alkali Metals. I. A. D. DOCK (*Chem. Weekblad*, 1908, 5, 529—551).—From aqueous solutions, the following hydrated thioantimonates of sodium, potassium, ammonium, and lithium have been isolated: $Na_3SbS_4 \cdot 9H_2O$; $K_3SbS_4 \cdot 6H_2O$; $K_3SbS_4 \cdot 5H_2O$; $Li_3SbS_4 \cdot 3H_2O$; $(NH_4)_3SbS_4 \cdot 4H_2O$, and $Li_3SbS_4 \cdot 10H_2O$. From aqueous alcoholic solutions, the following have been isolated: $Na_3SbS_4 \cdot 9H_2O$; $Li_3SbS_4 \cdot 5H_2O$; $K_3SbS_4 \cdot 3H_2O$; $(NH_4)_3SbS_4 \cdot 4H_2O$, and $Li_3SbS_4 \cdot 10H_2O$.

A. J. W.

Reaction between Ammonium Persulphate and Sodium Peroxide. R. KEMPF and ED. OEHLER (*Ber.*, 1908, 41, 2576—2580. Compare Abstr., 1906, ii, 19, 25).—The fact that when an aqueous alkaline solution of ammonium persulphate is kept for some time the ammonia formed is quantitatively oxidised to nitric acid, whereas when silver peroxide is present the main oxidation product is nitrogen, is accounted for by the different velocities of the two reactions, the latter being much more rapid than the former. If the first reaction is accelerated by raising the temperature, nitrogen is also formed.

Ammonium persulphate and sodium peroxide react readily. When the dry substances are rubbed together in a mortar, the mixture explodes, producing thick fumes. The same result is obtained by heating the mixture, by passing a stream of carbon dioxide over it, or by the addition of a drop or two of water. The temperature at which the explosion occurs lies between 75° and 140° , and depends on the rate of heating and the amount of moisture present. The gases evolved consist of nitrogen and oxygen, but the proportions vary considerably in different experiments.

The mixture is not explosive when the peroxide is replaced by sodium hydroxide, or the ammonium persulphate replaced by ammonium sulphate, sodium persulphate, or a mixture of the two.

J. J. S.

Hydrates of Baryta and Strontia. ROBERT DE FORCRAND (*Compt. rend.*, 1908, 147, 165—169. Compare this vol., ii, 153, 483).—The hydrate $\text{SrO} \cdot 9\text{H}_2\text{O}$ slowly loses water in a vacuum desiccator at 10° and, after a week, has the composition $\text{SrO} \cdot 2\text{H}_2\text{O}$. When left in a vacuum for a month, this is converted into $\text{SrO} \cdot \text{H}_2\text{O}$. The dihydrate, the existence of which has hitherto been questioned, is also formed by heating $\text{SrO} \cdot 9\text{H}_2\text{O}$ for two hours at $45\text{--}50^{\circ}$ in a stream of dry hydrogen; if the operation is carried out at 95° , the monohydrate is obtained in the same time, and this does not undergo further dehydration below 540° . At this temperature, however, water is lost until the product has a composition varying between $\text{SrO} \cdot 0.22\text{H}_2\text{O}$ and $\text{SrO} \cdot 0.06\text{H}_2\text{O}$. This has been mistaken by previous authors for anhydrous SrO , but it probably consists of a mixture of condensed hydrates. Anhydrous strontium oxide can only be obtained by heating this mixture to 850° for several hours.

The hydrate $\text{BaO} \cdot 9\text{H}_2\text{O}$ undergoes a somewhat similar series of changes when heated. The dihydrate, however, does not change into the monohydrate below $90\text{--}95^{\circ}$. $\text{BaO} \cdot \text{H}_2\text{O}$ has m. p. 325° , and does not lose water below 660° . When maintained at this temperature for several days, it becomes anhydrous; the change, however, is complete in two or three hours at 780° . There is no evidence for the existence of any compound intermediate between the monohydrate (hydroxide) and the oxide.

A table is given showing the heats of formation and heats of solution of the foregoing hydroxides and oxides in water, calculated from their heats of dissolution in dilute aqueous hydrogen chloride. The heat of solution for 1 gram molecule of SrO in 20 litres of water

at 15° is 29.76 Cal., and not 30.8 Cal. as previously stated by the author (*loc. cit.*). From these data, the following conclusions are drawn: (1) The conversion of $\text{SrO}, \text{H}_2\text{O}$ into SrO is more difficult than the conversion of $\text{BaO}, \text{H}_2\text{O}$ into BaO . (2) $\text{SrO}, 9\text{H}_2\text{O}$ and $\text{BaO}, 9\text{H}_2\text{O}$ should dissociate at 142° and 152° respectively, whereas the actual temperatures of dissociation are 102° and 107° . The difference of 40 – 50° is due therefore to an endothermic condensation of the molecule on the formation of the dihydrate. A further endothermic condensation occurs on the conversion of the dihydrate into the monohydrate. (3) The oxides should be represented as $(\text{SrO})_n$ and $(\text{BaO})_n$. W. O. W.

Action of Hydrochloric Acid on Manganese Dioxide. WILLIS B. HOLMES and E. V. MANUEL (*J. Amer. Chem. Soc.*, 1908, 30, 1192–1193. Compare Abstr., 1907, ii, 873).—The authors cannot as yet confirm the existence of manganese tetrachloride, although they have some evidence of the formation of a compound richer in chlorine than the trichloride. L. DE K.

Colour and Composition of Guignet's Green. LOTHAR WÖHLER and W. BECKER (*Zeitsch. angew. Chem.*, 1908, 21, 1600–1606).—Scheurer-Kestner's statement is confirmed (*Dingl. Polyt. J.*, 1865, 176, 386), that the boron present in Guignet's green is without influence on the colour, and is present only as a remnant of the chromium borate formed primarily by fusion of potassium dichromate with boric acid. By employing ammonium, instead of potassium, dichromate, Guignet's green is readily obtained free from boron, and has then the composition, $\text{Cr}_2\text{O}_3(\text{OH})_2$, ascribed to it by Scheurer-Kestner. The product obtained on heating potassium dichromate with an excess of boric acid has the composition $\text{Cr}_4\text{O}_3(\text{B}_4\text{O}_7)_3$.

Whilst Guignet's green has a vapour tension of 13 mm. at 75° , 16 mm. at 81° , and 26 mm. at 86° , the greyish-violet chromium hydroxide, which has the same composition, is found to have a vapour tension of only 2 mm., not increasing between 75° and 93.4° . This small vapour tension may result from the presence of moisture. These differences and the difference in colour of the two hydrates are ascribed to isomerism. The greyish-violet hydroxide is converted into its brilliant green isomeride on prolonged heating with water at 250° . G. Y.

Oxalate Reduction of Alkali Iridiochlorides. MARCEL DELÉPINE (*Compt. rend.*, 1908, 147, 198).—A reply to Vèzes' claim to priority (this vol., ii, 703). W. O. W.

Mineralogical Chemistry.

Fumaroles of Etna. Boric Acid in the Fumaroles of Vesuvius. ALFRED LACROIX (*Compt. rend.*, 1908, 147, 161–165).—The fumaroles of the recent (1908) eruption of Etna are of the same types as those of Vesuvius, but they are much less active; this is due

to the short period of the eruption, and to the fact that the magma was poor in volatile materials. The types specially described are: (i) fumaroles depositing alkali chlorides; (ii) those emitting hydrogen chloride and depositing krenersite, &c., and (iii) those depositing ammonium chloride alone. The crusts of ammonium chloride were found to contain small amounts of fluorine, perhaps present as an alkali silicofluoride.

In one of the fumaroles of the 1906 eruption of Vesuvius, a small amount of sassolite (H_3BO_3) in crystalline scales was detected. This is rare at Vesuvius, but its presence is of importance in connexion with theories of pneumatolytic action.

L. J. S.

Lavas of the Recent Eruption of Etna. ALFRED LACROIX (*Compt. rend.*, 1908, 147, 99—103).—The various products of the 1908 eruption of Etna were examined petrographically and chemically. They closely resemble one another in chemical composition and in the porphyritic crystals (of basic plagioclase, little augite and magnetite, and very little olivine) which they contain. The rock of a lava flow (anal. I) which has cooled more slowly, and has consequently crystallised more completely, contains in its ground-mass microlites of augite and olivine with very little glass; this rock is a basalt, or, according to the French terminology, a labradorite. In a slightly scoriaceous product (anal. II) of eruptions of the Strombolian type, and in a highly scoriaceous bomb (anal. III) resulting by an explosion of the Hawaiian type, the ground-mass contains more glassy material. Anal. IV is of the ash which fell during the eruption:

	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	Loss on igni- tion.	Total.
I.	49.75	18.59	6.28	3.45	9.76	4.96	1.89	2.15	0.03	0.40	100.13	
II.	49.71	18.40	1.93	6.96	3.45	9.80	5.13	1.72	2.58	0.62	0.70	99.70
III.	50.49	18.50	2.65	5.82	2.99	9.41	5.20	1.54	2.53	0.03	0.10	99.62
IV.	51.83	13.45	1.97	3.96	2.99	7.55	3.52	1.61	2.45	—	3.00	100.33

L. J. S.

Physiological Chemistry.

Blood coagulation Time. F. L. GOLLA (*Proc. physiol. Soc.*, 1908, lxi—lxii; *J. Physiol.*, 37). A modification of Buckmaster's coagulometer is described; it gives very constant results with a given blood. The coagulation time does not exhibit diurnal variation; it is not altered by fasting, or by the internal administration of sodium citrate or calcium salts. Nor is it abnormal in hæmophilia (1 case), purpura (1 case), or urticaria (2 cases). It is markedly prolonged in cases of jaundice, probably because of an alteration in the surface tension of the blood-film.

W. D. H.

Effect of Amyl Nitrite on Red Blood Corpuscles. GR. SLAVU (*Compt. rend.*, 1908, 147, 148—149).—Less than 0·3% of amyl nitrite does not produce a visible spectroscopic change in the blood. Death, after toxic doses have been administered, is not wholly due to want of oxygen, for a considerable quantity of the gas can be extracted from the blood in a vacuum. The oxygen which is set free, both *in vivo* and *in vitro*, is not derived from the plasma, but from the corpuscles.

G. B.

The Behaviour of the Sugar of the Blood after Bleeding. NILS ANDERSSON (*Biochem. Zeitsch.*, 1908, 12, 1—7).—The statement that the amount of sugar in the blood increases after bleeding is confirmed; this occurs in rabbits, especially after a second bleeding. The blood-sugar consists of 75% dextrose, and the remaining 25% is spoken of as residual sugar; it is not fermentable by yeast and gives a positive orcinol reaction, and so is probably a pentose, but this requires confirmation. Both varieties of sugar increase in the same proportion after bleeding; the total amount may be more than doubled.

W. D. H.

The Blood Issuing from the Dog's Suprarenal. F. A. YOUNG and J. E. LEHMANN (*Proc. physiol. Soc.*, 1908, liv; *J. Physiol.*, 37).—The blood issuing from the suprarenal gland, especially if it has been dammed back there for a time by a ligature, produces on injection into the general blood stream a decided rise of pressure, and so presumably contains adrenaline.

W. D. H.

Duration of Effect of Pituitary Extract on Blood Pressure. P. LOCKHART MUMFERY and W. LEGGE SYMES (*Proc. physiol. Soc.*, 1908, lvi; *J. Physiol.*, 37).—In the dog, the elevation of blood pressure produced by injection of pituitary extract may last twenty to thirty minutes; in the pithed cat, it may persist for many hours.

W. D. H.

Influence of Magnesium Sulphate on Metabolism. MATTHEW STEEL (*J. Biol. Chem.*, 1908, 5, 85—124).—Injection of magnesium sulphate into a muscle, or under the skin, does not cause diarrhoea. The total nitrogen eliminated is somewhat increased, but the most marked effect is the rise, relative and absolute, in urinary ammonia.

W. D. H.

Tolerance to Alcohol. JOSEF PRINGSHEIM (*Biochem. Zeitsch.*, 1908, 12, 143—152).—In animals accustomed to alcohol, the same quantity is excreted by lungs, kidneys, and skin as in those unaccustomed to its use. In both classes of animals, the faeces are free from alcohol. In both groups the amount united to glycuronic acid in the urine is the same, but that united to sulphuric acid is slightly higher in the "accustomed" animals. The "accustomed" animals burn off the alcohol more rapidly, that is, in about two-thirds of the time occupied in the burning by the "non-accustomed" group. In acute alcoholic poisoning, the percentage of alcohol in the body is

about 66% more in the "non-accustomed" animals. The seat of combustion is mainly the liver, then comes heart muscle, and the brain is last.

W. D. H.

Temperature-coefficients of Velocities of Various Physiological Actions. CHARLES D. SNYDER (*Amer. J. Physiol.*, 1908, 22, 309—334).—The large number of observations recorded and tabulated show that the temperature-velocities are all of magnitudes similar to those seen in physical and chemical reactions; in cases where it is known that metabolism occurs, the coefficients observed are those of chemical reactions; under this category are included the shortening of muscle, the latent period of smooth muscle, &c. Coefficients lower than these simulate physical actions, for instance, the latent period of striated muscle. In still other cases, the data are insufficient to draw conclusions from, as, for instance, the latent period of cardiac muscle and of vagus stimulation, and the velocity of urinary secretion and of lymph formation.

W. D. H.

Effects of Variations in Inorganic Salts and Reaction on Plants and Animals. BENJAMIN MOORE, HERBERT E. ROAF, and ROBERT E. KNOWLES (*Bio-Chem. J.*, 1908, 3, 279—312).—The range of ionic concentrations compatible with life is a narrow one. Short of the lethal dose, life and growth of plants are stimulated by alkali and not by acid. Potassium is more stimulating than sodium to both rootlets and flowers. The phosphatic anion causes increase in size, but irregularities in the flowers. In amphibia, both acid and alkaline phosphates increase growth. Higher concentrations cause death, which in the case of the alkaline salt is preceded by hyper-excitability. In mammals, alkaline and acid phosphates, in doses of 0.26—0.38 gram per kilo. of body-weight, cause increased metabolism, diminishing body-weight, and finally death. The adipose and muscular tissues waste considerably; other symptoms are polyuria, and with large doses, diarrhoea with ulceration of the alimentary canal, leucocytosis, degeneration of liver cells, and nephritis. The alkalinity of the serum is increased by the alkaline and diminished by the acid salt.

W. D. H.

Chemical Composition of the Herring during the Reproductive Period. THOMAS H. MILROY (*Bio-Chem. J.*, 1908, 3, 366—396).—The herring undoubtedly feeds until spawning time, and so differs from the salmon: the herring is therefore not dependent on its muscle proteins for the growth of its ovaries. In the male, as in the female, the highest fat percentage is found in the muscles just before rapid growth of the reproductive organs occurs; then it falls. The year may be divided into three periods: (1) The restitution or feeding period, three to four months before spawning; the spent fish recovers and accumulates a store of fat. (2) The ripening period, six to seven months. The fish still takes food, but in less amount, and the sexual organs grow as the store of muscle fat lessens. (3) The spawning period, two months; during this time feeding stops, the fat in the muscles falls greatly, and the water increases.

W. D. H.

Glycogen of Frog's Spawn. E. HAENSEL (*Biochem. Zeitsch.*, 1908, 12, 138—142).—Glycogen is present in frog's spawn in amounts varying from 0.016 to 0.052% of the fresh, or from 1.28 to 4.08% of the dry, material. The estimations were made by Pflüger's method. The addition of dextrose, lactose, or sucrose to the spawn causes a rise in the yield of glycogen. W. D. H.

Influence of Strontium on the Growth and Composition of Bone. HELENE STOELTZNER (*Biochem. Zeitsch.*, 1908, 12, 119—137).—The experiments recorded on growing dogs show that if the diet is poor in calcium, or if the calcium is partly replaced by strontium, the bone condition that results differs from that seen in rickets; in the latter condition, the relationship of calcium to fat-free dry substance is lessened, but this was not the case in the experimental puppies. Strontium is laid down in the bone in relatively important amount, but it does not seem able to take the place of calcium in producing healthy bone. W. D. H.

Chemistry of Muscle and Liver of Reptiles. JOHN F. LYMAN (*J. Biol. Chem.*, 1908, 5, 125—127).—Four kilograms of fresh muscle and the livers from two pythons were examined. From the muscle, creatine and sarcosine were separated and identified. The most conspicuous purine derivative is hypoxanthine, as in higher vertebrates.

From the livers, uric acid, guanine, and adenine were obtained. Xanthine and hypoxanthine could not be separated in amounts sufficient for identification. W. D. H.

Contraction of Muscles in Relation to the Presence of Receptive Substances. II. JOHN N. LANGLEY (*J. Physiol.*, 1908, 37, 165—212. Compare this vol., ii, 120).—Further details of the phenomena of nicotine poisoning in frog's muscle, which support the author's previous contention that there exist in the muscle, or its nerve-endings, or both, substances with which the nicotine combines. W. D. H.

Cholesterol in Coelenterata. CHARLES DORÉE (*Proc. physiol. Soc.*, 1908, lviii—lix; *J. Physiol.*, 37).—Cholesterol is generally regarded as a constant constituent of cell protoplasm. It is certainly present in sea-anemones. W. D. H.

Kidney Secretion of Indigo carmin, Methylene-blue, and Sodium Carminate. GEORGE D. SHAFER (*Amer. J. Physiol.*, 1908, 22, 335—352).—The experiments recorded confirm Heidenhain's views on urinary formation; indigo-carmin, leuco-indigo-carmin, and methylene-blue are secreted at varying rates by the convoluted tubules and the wider limb of Henle's loop. Sodium carminate, on the other hand, passes out by the glomeruli. W. D. H.

[Symptomatic] Significance of Urinary Indoxyl. Detection of Indole in Pus. CHARLES PORCHER (*Compt. rend.*, 1908, 147, 214—217).—Pus, diluted with water and made alkaline, is distilled with steam; the indole is extracted from the distillate by pure

benzene, in which it is detected by the colour reaction with *p*-dimethyl-aminobenzaldehyde. In less than half the number of specimens examined, indole was present; its formation seems to depend on the presence of particular organisms.

G. B.

Renal Calculi. J. SYDNEY ROWLANDS (*Bio-Chem. J.*, 1908, 3, 346—350).—A series of twenty-two calculi from South-west Lancashire and North Wales was examined. The commonest constituent was found to be calcium oxalate. Uric acid was rare, and was absent in nineteen cases.

W. D. H.

Concentration of Diphtheria Toxin. P. G. HEINEMANN (*J. Biol. Chem.*, 1908, 5, 27—30).—A high potency diphtheria toxin is advantageous in the production of diphtheria antitoxin. Concentration of the former by precipitating with alcohol or salts of heavy metals is accompanied by loss of potency; this, however, is minimised by the use of neutral salts as the precipitating agent. In the present research, ammonium sulphate was used; the salt was subsequently removed by dialysis through heavy parchment. Phenol was then added to the re-dissolved precipitate as a preservative to the extent of 0.3%; more than this precipitates the toxin. The loss of potency is very slight.

W. D. H.

Experimental Glycosuria. II. Glycogenolytic Fibres in the Great Splanchnic Nerve. JOHN J. R. MACLEOD. **III. Influence of Stimulation of the Great Splanchnic Nerve when the Liver is Deprived of its Blood Supply.** JOHN J. R. MACLEOD and H. O. RUIR (*Amer. J. Physiol.*, 1908, 22, 397—409).—Stimulation of the great splanchnic nerve in dogs produces marked hyperglycemia within half an hour, accompanied by diuresis and glycosuria. If the stimulation is continued for hours, these effects reach a maximum in about two hours and then decline. Liberal administration of oxygen lessens, but does not abolish, the effect; atropine, also, does not prevent the effect. Ligature of the hepatic artery or clamping of the portal vein do not in themselves produce hyperglycemia. The glycogen which disappears from the liver is greater in amount when the nerve is stimulated when the portal blood is diverted into the inferior vena cava than when the stimulation is omitted. This, however, is not conclusive evidence in favour of glycogenolytic secretory fibres, for the stimulation might produce bloodlessness of the liver by constricting the hepatic artery. If, however, the glycogen still disappears during stimulation of the nerve, when the liver is rendered completely anæmic by ligature of the portal vein and hepatic artery, then the existence of such nerve-fibres is definitely proved. In two out of three experiments, the disappearance was greater during a ten minute period of stimulation than in the preceding ten minutes when no stimulation was employed. If no stimulation is used at all, the rate of disappearance during the second ten minutes is the same as, or less than, that occurring during the first period.

W. D. H.

Calcium Metabolism in Relation to Rickets. HANS ARON (*Biochem. Zeitsch.*, 1908, 12, 28—77).—A critical and experimental review of calcium metabolism in relation to the aetiology of rickets. The lack of calcium may be due to the small amount in the food, or to its non-absorption, or to its too rapid excretion. The experiments recorded on animals, together with observations on human infants, show the overwhelming importance of the first of these three factors. The effect falls mainly on the skeletal structures, for the amount of calcium may remain normal in other organs. Among the interesting points raised are: (1) the pooriness of human milk in calcium, and the suggestion is made that weaning should occur at an earlier date than that usually laid down; and (2) the fact that the milk of mothers of rickety children is poorer in calcium than that of other women in relation to the organic constituents in the milk. Doubtless other factors also step in, especially rapidity of growth in such children.

W. D. H.

Arsenic and Trypanosomes. MARTIN JACOBY and ALBERT SCHÜTZE (*Biochem. Zeitsch.*, 1908, 12, 193—202).—Phagocytosis does not appear to be a factor in the defence of the body against trypanosomes, and the beneficial influence of arsenic is not due to its stimulating leucocytic activity, but rather to its direct influence on the parasites.

W. D. H.

Pharmacological Action of cycloHexane and Some of its Derivatives. A. BRISSEMORET and J. CHEVALIER (*Compt. rend.*, 1908, 147, 217—219).—A comparison of the action of cyclohexane, cyclohexanol, *i*-quercitol, and inositol on the action of the isolated rabbit's heart perfused with Locke's solution. The primary effect (contraction of the heart's muscle) of all four substances is attributed to their having a common carbon skeleton. With cyclohexane, and especially with cyclohexanol, the toxic effect on the nerves of the heart is most prominent.

G. B.

[Physiological] Action of Substances of the Saponin Group. LEONHARD WACKER (*Biochem. Zeitsch.*, 1908, 12, 8—14).—Substances of the saponin group obtained from various plants appear to differ in toxicity; the experiments recorded (on dogs) were performed with a mixture of quillajic acid and sapotoxin. Deleterious effects on the kidney are described. The toxic action on the blood is less if the drug is given by the mouth, and the addition of extracts of the intestinal mucous membrane to solutions outside the body lessens their hæmolytic properties; the gastric mucous membrane is even more powerful in the same direction.

W. D. H.

Absorption of Certain Poisonous Gases by the Respiratory Tract. KARL B. LEHMANN, JOSEPH WIENER, JOHANNES WILLKE, and JIRO YAMADA (*Arch. Hygiene*, 1908, 67, 57—98).—If the air contains from 0.2 to 0.3% of ammonia, from 80 to 90% of this is absorbed, and absorption is mainly brought about by the nasal and buccal mucous membranes. If the mixture is passed directly into the lungs of an

animal, about 56% of the ammonia is absorbed, but it is not possible to say whether the absorption occurs in the bronchial tubes or in the alveoli.

Hydrogen chloride is absorbed by the nose and trachea to the extent of 60—75%. An animal in this way absorbed 252 milligrams of the gas in an hour, sufficient to produce acid poisoning; injury to the mucous membrane is also readily produced. Sulphur dioxide is absorbed by the same channels to the extent of 35—58%. It is relatively more toxic than hydrogen chloride. Acetic acid vapour is less toxic than hydrogen chloride. It produces hyperemia and acidity of the mucous membrane, but no hæmorrhage. The amount absorbed varies from 62 to 86%. A few experiments on carbon disulphide are also given; the amount absorbed is about 20—22%. Full analytical details are given throughout; the experiments on animals were supplemented throughout by experiments on man.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Action of Heavy Metals on *Bacillus Typhorus*. BENJAMIN MOORE and JAMES LEONARD HAWKES (*Bio Chem. J.*, 1908, 3, 313—345).—The investigation was undertaken on fresh-water mussels with a view to their purification from the bacillus of typhoid fever. Ferrous sulphate and ferric chloride solutions (1 in 1000) act beneficially on the mussels, and kill all the bacilli in twenty-five hours. Salts of silver, copper, zinc, and lead were found to be useless; they either act detrimentally on the mussels, or do not free them from the bacilli in a reasonable time.

W. D. H.

Fermentation of Malic Acid in the Production of Wine. AUGUSTE ROSENSTIEHL (*Compt. rend.*, 1908, 147, 150—153. Compare *Mestrezat*, this vol., ii, 723). Malic acid is transformed into lactic acid and carbon dioxide by *Micrococcus malolacticus* occurring in the grape: in order to secure proper ripening of the wine, this bacillus should not be allowed to develop rapidly, so that the malic acid disappears slowly.

G. D.

Fermentation of Calcium Tartrate. OSKAR EMMERLING (*Centr. Bakt. J'ar.*, 1908, ii, 21, 317—318).—The experiments were made with a *Spirillum* found in the waste waters from a tannery. When inoculated into a culture solution containing inorganic and organic food substances and solid calcium tartrate, it was found to decompose the latter salt quantitatively, giving rise to calcium carbonate and carbon dioxide. Thus, in one experiment, 5 grams of the tartrate were originally put into the solution, of which 4.3 were decomposed, giving rise to 2.05 grams of calcium carbonate (theor. = 2.2 grams). Decomposition proceeds more rapidly the greater the surface of liquid exposed to the air and the more frequently the liquid is shaken.

In all fermentations of calcium tartrate studied previously, the reaction has been more complex, and has given rise to several fatty acids.
E. J. R.

Influence of the Sterilisation Temperature of Grape Juice and of the Fermentation Temperature on the "Bouquet" of Wine. AUGUSTE ROSENSTIEHL (*Compt. rend.*, 1908, 146, 1417—1420).—The best temperature for sterilisation is 50—52°; at 55—60° the bouquet suffers. It is true that at the lower temperature only a partial sterilisation is achieved, but below 26° the surviving yeast cells do not appreciably resume their growth in the first forty-eight hours, so that there is time for the pure culture, with which it is desired to conduct the fermentation, to establish itself. A further reason for conducting the fermentation at a low temperature (20°) is that at a higher temperature the carbon dioxide evolved carries away substances the scent of which makes up the bouquet. The gases given off may be passed into sterile grape juice, to which they communicate the bouquet.
G. B.

De-amidising Ferments of Fungi. HANS PRINGSHEIM (*Biochem. Zeitsch.*, 1908, 12, 15—25).—Various fungi, such as yeast and *Aspergillus niger*, have the property of liberating ammonia from nitrogenous substances, especially from amino-acids. This is due to enzymatic action. After treatment with acetone and ether, this property is lost. The de-amidised residue is changed into alcohols, with the evolution of carbon dioxide, by an enzyme contained in yeast, which is also killed by acetone and ether. The theoretical bearing on these facts in relation to the growth of fungi is discussed.
W. D. H.

Influence of the Concentration of Sugar Solutions on Respiration [of Seedlings]. A. MAUGE and G. NICOLAS (*Compt. rend.*, 1908, 147, 139—142).—Bean seedlings placed for fifteen to twenty-two hours in sugar solutions of various concentrations (up to 10%) showed increased intensity of respiration, both normal and intramolecular. With all sugars examined, except lactose, the respiration increases progressively with the concentration.
G. B.

Behaviour of Certain Organic Substances in Plants. I. GIACOMO L. CIAMICIAN and C. RAVENNA (*Gazzetta*, 1908, 38, i, 682—697).—The glucosides amygdalin, salicin, and arbutin are tolerated by maize and French beans to a much greater extent than the aromatic substances present in the glucosides, namely, benzaldehyde, saligenin, and quinol. The plants into which the latter are introduced die within three days, whilst those treated with the glucosides reach complete maturation. In a period of two months, a single plant can be treated with as much as 3 grams of glucoside without injury.

The glucosides introduced into the plants undergo partial hydrolysis, and are apparently utilised by the plants, since extraction of the latter only yields a fraction of the total glucoside introduced.

T. H. P.

Mechanism of the Distribution of Odoriferous Principles in Plants. EUGENE CHARABOT and G. LALOUÉ (*Compt. rend.*, 1908, 147, 144—145).—In general, those constituents of an essential oil which are most soluble in water are most readily transported from the leaves to the flowers. Menthol is more soluble than menthone, yet in peppermint plants the flowers contain more menthone than the leaves. This is, however, the result of oxidation of the menthol after it has been transported into the flowers, and therefore a secondary effect.

G. B.

Chemical Changes Consequent on the Wounding of Plants. RUDOLF FRIEDRICH (*Centr. Bakt. Par.*, 1908, ii, 21, 330—347).—The author gives a full résumé of previous work on the subject, dealing especially with (a) the increased evolution of carbon dioxide, (b) the increased production of protein, in wounded potatoes and onions. He finds that the former of these phenomena is also shown by other parts of plants (leaves, fruit, &c.), but not always the latter; thus potatoes and oak leaves respectively gave the following results:

	Total N.	Protein N.	Amide N.	Carbo- hydrate.	Acidity.
Potatoes (tubers), wounded	1.476	1.250	0.123	70.240	21.350
" not wounded	1.301	0.888	0.167	73.820	21.430
Oak leaves, wounded	5.171	3.557	1.230	8.191	30.530
" not wounded	5.392	3.198	1.004	12.420	48.800

The figures refer to percentages on the dry substance.

The fall in carbohydrate is correlated with the increased respiration, but the increase in acidity is not discussed, since the acids actually produced were not investigated. It was found that the protein production in the wounded potato, onion, and pear depended on the presence of the large amount of carbohydrate; the fruits of *Cydonia japonica* and leaves of *Clivia Gardneri*, which behaved like oak leaves, contained only small quantities. This observation lends support to Pfeffer's view that protein is formed from plants by a reaction between carbohydrate and amide material.

E. J. R.

Origin of the Colouring Matter of Red Grapes and of Other Plant Organs. J. LABOUZ (*Compt. rend.*, 1908, 146, 1411—1413*).—By heating the solid parts of young, green grapes with 2% hydrochloric acid to 120° for thirty minutes, a red colouring matter is formed from the tannins. A similar pigment may be formed by boiling with alkali in the presence of air.

G. B.

Oxydase in the Latex of *Hevea Brasiliensis*. DAVID SPENCE (*Bio Chem. J.*, 1908, 3, 351—352).—Four samples of this latex (Para rubber) gave marked evidence of the presence of an oxidising enzyme.

W. D. H.

Ripening of Tomatoes (*Lycopersicum esculentum*). F. M. ALMAHARY (*Compt. rend.*, 1908, 147, 146—147).—During ripening, a considerable increase in the amount of organic acids, sugars, starch, and non-protein nitrogenous substances takes place, whilst proteins and cellulose diminish.

G. B.

* and *Bull. Assoc. chim. Sac. Dist.*, 1908, 26, 76—78.

Physiological Action of Dicyanodiamide. OSCAR LOEW (*Chem. Zeit.*, 1908, 32, 676—677).—Whilst under ordinary conditions calcium cyanamide decomposes entirely into calcium and ammonium carbonates, in alkaline soils there is a possibility of a partial production of dicyanodiamide. According to Ulpiani and Perotti (*Abstr.*, 1907, ii, 295), the latter compound is not poisonous to crops, and may even be employed as a source of nitrogen; Kappen showed that it is very slowly converted into ammonia.

Experiments in which young barley plants (14—16 cm. high) were placed in a 0.5% solution of dicyanodiamide showed an injurious action after two days. In the case of small *Lathyrus* plants, no injurious action was observed until several days later, owing, perhaps, to evaporation being less. With 0.05—0.1% solutions, only the points of the leaves were affected; solutions of guanidine hydrochloride of the same strength killed barley plants in a few days.

Further experiments with twigs of *Tradescantia* in 0.1%, and *Elodea* in 0.2% solutions of dicyanodiamide showed that no injurious effect was produced in either case, and that *Elodea* utilised dicyanodiamide as a source of nitrogen. The poisonous effects observed by Immendorff and Wagner were, perhaps, due to some decomposition product. Threads of *Spirogyra* in 1% solutions of dicyanodiamide remained intact for several days; worms lived for more than four days in 0.5% solutions. Bacteria in broth containing 0.5% were not injured in the least.

As regards the constitution of dicyanodiamide, it is suggested that the imide ring formula (Baumann) best accords with its slightly acid character and with its physiological properties, as compared with dicyanodiamidine and guanidine.

N. H. J. M.

Analytical Chemistry.

Automatic Safety Burette. GUSTAV MÜLLER and O. BERGMAN (*Chem. Zeit.*, 1908, 32, 711).—A modification of the apparatus described previously (this vol., ii, 626). The reservoir has been replaced by a tube connected with a large container. The circulation tube is replaced by an overflow chamber fitted with an open conical lid, which is firmly tied to it by means of glass hooks and strong rubber bands. A float, terminating in a cone, serves as a valve, which closes when, after filling the burette, sufficient liquid has entered the overflow chamber.

L. DE K.

Detection of Fluorine Compounds in Wines. L. VANDAM (*Ann. Chim. anal.*, 1908, 13, 260—262).—A reply to Carles (this vol., i, 318). The author proves that the amount of fluorine in oenological products is too small to interfere with the use of his process (this vol., i, 631).

L. DE K.

Apparatus for the Quantitative Distillation of Ammonia. PHILIP A. KOBER' (*J. Amer. Chem. Soc.*, 1908, 30, 1131—1135).—The author has applied Folin's process to the Kjeldahl nitrogen estimations. The fused mass in the Kjeldahl flask, when sufficiently cooled, is mixed with 40—90 c.c. of water (about 4 vols. of water to 1 vol. of sulphuric acid present), and the flask is connected with two cylinders, one containing an amount of aqueous sodium hydroxide more than sufficient to neutralise all the sulphuric acid, and the other, a standard solution of sulphuric acid to absorb the ammonia given off. By applying suction, the alkali is forced into the flask, and the heat developed is sufficient to expel all the ammonia. When all the alkali has been carried over, the cylinder may be disconnected and replaced by an arrangement for supplying ammonia-free air. The suction is continued until the contents of the flask are perfectly cooled down.

L. DE K.

Folin's Method of Estimating Ammonia in Urine. MATTHEW STEEL and WILLIAM J. GIES (*J. Biol. Chem.*, 1908, 5, 71—84).—Certain urines, collected during metabolism experiments with magnesium sulphate, gave discordant results when the ammonia in them was estimated by Folin's method. This is due to the fact that relatively large quantities of ammonio-magnesium phosphate are eliminated under these conditions, some of it being deposited in crystalline form; this deposit is not thoroughly decomposed by sodium carbonate as used in Folin's process, and so a variable amount of ammonia is lost.

W. D. H.

Limitations of the Copper-Zinc Couple Method in Estimating Nitrates. JOHN E. PURVIS and R. M. COURTAULD (*Proc. Camb. Phil. Soc.*, 1908, 14, 441—446).—The authors have examined the accuracy of the copper-zinc couple method of estimating nitrates and nitrites in waters which contain considerable quantities of organic nitrogen compounds, such as soluble peptones, blood-serum, and soluble albumin. From a comparison of the results with those of blank experiments, it is found that the organic nitrogen is to some extent reduced to ammonia under the influence of the couple. Similar results were obtained with a sample of sewage to which known quantities of potassium nitrate were added. It is suggested that the reduction of the organic nitrogen is not merely due to the hydrogen liberated by the couple, but is influenced by the oxygen liberated simultaneously by the electrolytic action.

H. M. D.

The Nitro-Molybdate Method for the Detection of Phosphorus in Tissues. G. G. NASMITH and E. FIDLER (*J. Physiol.*, 1908, 37, 278—284). In agreement with Macallum, but contrary to the view of Scott, the cold nitric acid employed does separate inorganic phosphates from nucleins and nucleic acids. Bensley's view is acquiesced in that the reduction of compounds of molybdenum is the cause of the bluish green colour which appears in microscopic preparations, and that it is not due to the presence of phosphorus at all.

W. D. H.

Estimation of Phosphoric Acid. NORBERT VON LORENZ (*Chem. Zeit.*, 1908, 32, 707—709).—A defence of the author's method (direct weighing as ammonium phosphomolybdate), which is applicable in all cases, whereas the citrate process gives but indifferent results.

L. DE K.

Microchemical Analysis. III. Arsenic, Antimony, Tin. NICOLAAS SCHOORL (*Zeitsch. anal. Chem.*, 1908, 47, 367—389. Compare this vol., ii, 432).—The process is based on the characteristic microscopical appearance of arsenious acid, ammonium calcium arsenate, ammonium magnesium arsenate, and arsenic iodide. Antimony may be isolated as caesium antimony chloride or, preferably, iodide, or as sodium antimonate, whilst tin yields characteristic compounds with caesium and rubidium chlorides, all of which are readily detected microscopically.

Tin and antimony are conveniently separated from arsenic by heating the mixed sulphides obtained in the ordinary course of analysis with 25% hydrochloric acid, which leaves the arsenic practically undissolved. A portion of the filtrate is then tested for tin with rubidium chloride, and another portion for antimony with caesium chloride and potassium iodide. The arsenic is oxidised with nitrohydrochloric acid, and then converted into the magnesium compound.

L. DE K.

Separation of Lithium Chloride from the other Alkali Chlorides and Barium Chloride. LOUIS KAHLENBERG and FRANCIS C. KRAUSKOFF (*J. Amer. Chem. Soc.*, 1908, 30, 1104—1115).—The solution of the mixed chlorides is evaporated just to dryness, and the residue, which should not exceed 2 grams, is boiled for a few minutes with 25 c.c. of pyridine; any large particles are crushed with a stirring rod. The clear liquid is decanted through a small filter, and the insoluble matter washed twice with a little hot pyridine. It is then dissolved in a little water, evaporated to bare dryness, and again extracted with hot pyridine. The pyridine filtrates, which contain all the lithium chloride, are mixed, the bulk of the pyridine is recovered by distillation, and the lithium chloride is converted into sulphate by evaporation with sulphuric acid and weighed as such.

L. DE K.

Assay of Telluride Ores. GEORGE BORROWMAN (*J. Amer. Chem. Soc.*, 1908, 30, 1023—1027).—The irregularities in the assay of high-grade auriferous tellurides are due to lack of homogeneity of the sample, and not, as has been suggested, to the tellurium. In some cases, however, it is advisable to remove the tellurium with nitric acid. Any silver is then precipitated as chloride, and added to the insoluble residue, which is then assayed as usual for gold and silver. The most favourable temperature is about 1200°.

L. DE K.

Evaluation of [Commercial] Red Lead. P. BECK (*Zeitsch. anal. Chem.*, 1908, 74, 465—492).—An exhaustive research as to the most trustworthy methods for the analysis of red lead. The author gives the following summary.

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The red lead may be dissolved in dilute nitric acid, and separated from insoluble impurities by the use of such reducing agents as sucrose, oxalic acid, lactic acid, methyl alcohol, formaldehyde, glycerol, phenylhydrazine, salts of hydroxylamine, but best of all by hydrogen peroxide.

When small quantities only are available, Bunsen's process (distillation with hydrochloric acid and estimation of the chlorine liberated) may be used, but in works, Topf's process (titration of iodine liberated from potassium iodide with sodium thio-sulphate) should be used, as this allows the use of 5 grams of the sample. I. DE K.

Solubilities of the Oxalates of the Rare Earths. I. Solubility of the Oxalates of Lanthanum, Cerium, and Samarium in dilute Sulphuric and Oxalic Acids or their Mixtures. OTTO HAUSER and FRITZ WIRTH (*Zeitsch. anal. Chem.*, 1908, 47, 389-400).—Tables showing the solubility of the oxalates of the cerium group in dilute sulphuric and oxalic acids, and in a mixture of the two; the strength of the acids varies from 0.05*N* to 4.3*N*.

As a result of this investigation, the following process is recommended. The rare earths are separated from accompanying alkaline earths by precipitation with ammonium chloride and pure ammonia. The washed precipitate is dissolved in hydrochloric acid, and, after expelling the excess by evaporation, the residue is dissolved in about 60 parts of *N* 4—*N* 2 sulphuric or hydrochloric acid. A saturated solution of oxalic acid is then added in such quantity that the solution will contain about 3% of that acid. If lanthanum is present in large excess, ammonium oxalate should be used. In presence of more acid, the process becomes quite inaccurate for lanthanum, and less accurate for cerium. I. DE K.

Influence of Fine Grinding on the Water and Ferrous Iron Content of Minerals and Rocks. WILLIAM F. HILLEBRAND (*J. Amer. Chem. Soc.*, 1908, 30, 1129-1131).—A series of tabulated experiments on the influence of fine grinding on minerals containing ferrous iron and on the iron and water content. In order to avoid oxidation, it is recommended that the grinding should be effected under alcohol, or, better still, the coarse powder should be treated directly with hydrofluoric acid and the solution titrated for ferrous iron; any undissolved matter is then finely ground under water, and again treated with hydrofluoric and sulphuric acids (for details, compare *Bull.* 305, *U.S. Geol. Survey*, 1912). I. DE K.

Volumetric Estimation of Iron and Chromium by means of Titanous Chloride. S. B. JALAR (*J. Soc. Chem. Ind.*, 1908, 27, 673-674). The principles involved in the method are: (1) hydrogen peroxide oxidizes chromium salts in alkaline solutions to chromates, these becoming dichromates on acidifying the solutions; (2) hydrogen peroxide reduces dichromates to chromates in acid solutions, ferric salts being unchanged; (3) on titrating a mixture of a dichromate and a ferric salt, for all practical purposes the dichromate is reduced first

the colour change marking the reduction and the ferric salt being left in solution. Of these, the first one is involved in bringing the iron and chromium in an ore into solution; on the second and third, the following process depends. A weighed quantity of about 0.5 gram of the finely powdered ore is fused with a mixture of sodium hydroxide and sodium peroxide, more of the latter being added subsequently. After cooling, the fused mass is extracted with water, the solution is boiled to remove all traces of hydrogen peroxide, then acidified with sulphuric acid, and again boiled and diluted to a volume of 500 c.c. Fifty c.c. of the solution are titrated with standardised titanous chloride solution until a clear violet coloration is obtained, showing that all the dichromate is reduced; a few more drops of titanous chloride are added to make sure that only the ferric salt remains in solution, then a few drops of thiocyanate solution are added as indicator, and the solution is titrated until the colour disappears. The volume of titanous chloride solution used represents the dichromate and iron together. A second 50 c.c. of the solution are treated with hydrogen peroxide to reduce the dichromate, and the mixture is boiled to expel the excess of hydrogen peroxide. When cold, the solution is titrated with titanous chloride solution, a few drops of thiocyanate solution being added as an indicator. In this titration, the volume of titanous chloride used represents the amount of iron only. A sensitive indicator may be prepared by adding a few drops of potassium thiocyanate solution to a dilute ferrous sulphate solution.

W. P. S.

Estimation of Nickel and Chromium in Steel. EDWARD D. CAMPELL and WALTER ARTHUR (*J. Amer. Chem. Soc.*, 1908, 30, 1116—1120).—A modification of Moore's process. One gram of the sample is converted into sulphate by evaporating with nitric acid and sulphuric acid, and to the solution, measuring about 70 c.c., 13 grams of sodium pyrophosphate dissolved in 70 c.c. of hot water are added. This is preferable to the citric acid usually employed. The precipitate is dissolved by cautious addition of ammonia, and warming towards the end.

Five c.c. of 0.05% silver nitrate and then 5 c.c. of 2% potassium iodide are added, and standardised potassium cyanide is run in until a clear liquid has been obtained. If copper is present, it must be remembered that 1 part of this counts for $\frac{3}{4}$ part of nickel. Copper, however, may be left undissolved by avoiding the use of nitric acid. If chromium is also present, it must be rendered harmless by oxidation with potassium permanganate before adding the pyrophosphate. If chromium only has to be estimated, the chromic acid thus formed is titrated in the usual way with ferrous ammonium sulphate and permanganate.

L. DE K.

Separation of Tungsten from Chromium. Estimation of Tungsten in Steel containing Chromium. GEORG VON KNORRE (*Zeitsch. anal. Chem.*, 1908, 47, 337—366).—1.5—6 Grams of the sample are dissolved in a small quantity of dilute hydrochloric acid. When no further action takes place on boiling, the excess of acid is at

once neutralised with sodium hydroxide, and, when cold, 8–10 c.c. of *N*.10 sulphuric acid are added, and then, without previous filtration, 30–60 c.c. of benzidine reagent (20 grams of benzidine and 25 c.c. of concentrated hydrochloric acid per litre). The precipitate, which contains all the tungsten, also more or less chromium, is washed with the diluted reagent and burnt in a platinum crucible. The ash is then fused with sodium carbonate, and the mass extracted with water. The filtrate is acidified with hydrochloric acid, using methyl-orange as indicator, and then boiled for some time to convert the tungsten into metatungstic acid. When cold, the chromic acid is reduced by a solution of sulphur dioxide, and the tungsten precipitated with excess of the benzidine reagent. Addition of sulphuric acid is, as a rule, unnecessary, as enough is formed owing to the oxidation of the sulphur dioxide. On ignition, pure tungsten trioxide is obtained.

L. DE K.

Volumetric Estimation of Titanium. GINO GALLO (*Gazzetta*, 1908, 38, i, 658–659. Compare Abstr., 1907, ii, 402, and Knecht and Hibbert, Abstr., 1903, ii, 509).—Titanium is usually accompanied by iron, so that the method given by Newton (this vol., ii, 325) for the volumetric estimation of titanium is inapplicable in practice.

T. H. P.

Purity and Volatility of Precipitated Antimony Sulphide. LEWIS A. YOUTZ (*J. Amer. Chem. Soc.*, 1908, 30, 975–979).—Antimony sulphide precipitated from a solution containing free hydrochloric acid is never pure, but is always contaminated with more or less antimony oxychloride, which cannot be removed even by redissolving the precipitate in ammonium sulphide and reprecipitating with acetic acid. In practice, this admixture does not interfere with the accuracy of the analysis if care is taken to heat the precipitate in an atmosphere of carbon dioxide at 250° only just long enough to transform it into the black sulphide; a prolonged heating causes volatilisation of the antimony oxychloride, and consequent loss.

Antimony sulphide precipitated from a solution free from chlorides does not suffer loss on prolonged heating at 250° in a current of carbon dioxide.

L. DE K.

Electrolytic Estimation of Bismuth. J. PESET (*Zeitsch. anal. Chem.*, 1908, 47, 401).—0.04–0.08 Gram of a bismuth salt is heated with 4–5 c.c. of water and 3 c.c. of sulphuric acid, and, when all is dissolved, the solution is diluted to 140 c.c. and submitted to electrolysis, using a rotating anode. Conditions: 2 volts; 0.002 to 0.01 ampere; temperature, 50°; time, eighteen to twenty hours. When the solution is quite free from bismuth, 0.08–0.15 gram of accurately weighed cadmium sulphate dissolved in 10 c.c. of water is added, and the electrolysis is continued now under the following conditions: 2.5–3.5 volts; 0.2–0.3 ampere; time, eight hours.

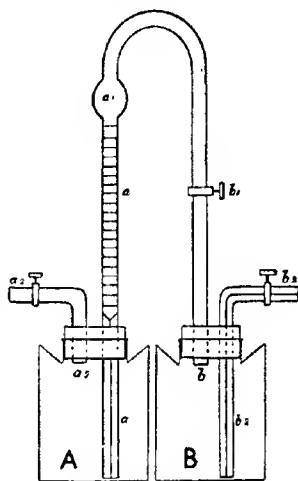
The calcium thoroughly protects the bismuth from oxidation, and renders it more adhesive.

L. DE K.

Simple Form of Apparatus for Observing the Rate of Absorption of Oxygen by Polluted Waters and by other Fermenting Liquids. WALTER E. ADENEY (*Sci. Proc. Roy. Dubl. Soc.*, 1908, 11, 280—287).—It has

been shown (Abstr., 1896, ii, 322; 1898, ii, 86; 1902, ii, 221) that the determination of the extent and rate of absorption of oxygen is of fundamental importance in the examination of polluted waters.

A simple apparatus for carrying out these determinations has now been devised, and is figured in the accompanying diagram. Flask *B* is charged with the polluted water and *A* with distilled water. The taps *a*₂ and *b*₂ being closed, absorption takes place in *B*, but not in *A*, which acts therefore as a standard pressure gauge. The difference of pressure read off on the graduated tube *a*, in which the distilled water rises when *b*₁ is opened, shows the amount of absorption in *B*. The original should be consulted for details as to the size of the apparatus, the method of use, and the manner of calculating the results.



G. Y.

Detection of Free Acids in Organic Liquids. FERNAND REPERTON (*Ann. Chim. anal.*, 1908, 13, 269—270).—Five c.c. of Fehling's solution are boiled in a test-tube, and, if no change takes place, a few drops of the solution to be tested for acidity are added, when a precipitation of copper oxide takes place. One drop of an *N*/10 acid solution will give the test.

L. DE K.

Physico-chemical Analysis of Wines. PAUL DUTOIT and MARCEL DUBOIX (*Compt. rend.*, 1908, 147, 134—137).—A strong solution of baryta is added in small portions to the wine, the conductivity of which is measured after each addition. At first the conductivity falls, and a sharp minimum indicates the point at which all the sulphates have been precipitated. It then rises to a maximum, corresponding with neutrality to litmus. On further addition of baryta, a gelatinous precipitate occurs, and the curve of conductivity shows a shallow dip, the length of which is a measure of the amount of tannins present. After this, the conductivity rises in a straight line. In one operation, three constituents of the wine are thus determined, the sulphates and acids with great accuracy.

G. B.

Origin and Variations of Sulphates in Beer. Interpretation of Analytical Results. ACHILLE MÜNTZ and J. AUGUSTE TRILLAT (*Ann. Chim. anal.*, 1908, 13, 253—260).—An investigation to ascertain whether the presence of more than 2 grams of potassium sulphate per litre in beer should be called adulteration. The authors point out that even more than 2 grams may be fully accounted for by the sulphate derived from the water (Burton water, for instance) and the other materials used in the brewing process. The potassium is derived mainly from the malt, and is often present in sufficient quantity to cover the sulphate fully; the authors, however, doubt whether even then it is really permissible to calculate and report all the SO_4 found as potassium sulphate.

A further quantity of sulphate is due to the sulpinning of the hops or from the use of sulphites; a special test should be made to detect the latter.

L. DE K.

Detection of Thiocyanic Acid by means of Mercurous Chloride. EGINO POLIACCI (*Chem. Zentr.*, 1908, i, 1576; from *Arch. Farmacol. speriment.*, 7, 94—96).—To detect thiocyanic acid in saliva, 12—15 c.c. are warmed with 40—42 c.c. of absolute alcohol, the filtrate is concentrated to 6—7 c.c., and the residue again filtered. On adding mercurous chloride, this will be reduced in the cold to metallic mercury, which reaction is characteristic for thiocyanic acid. The process may be applied also to solid animal matter.

L. DE K.

Estimation of Citral in Lemon-grass Oil. ARMAND BLOCH (*Chem. Zentr.*, 1908, i, 1500; from *Bull. Sci. Pharmacol.*, 1908, 15, 72—77).—Ten c.c. of the sample are introduced into a 100 c.c. flask, the neck of which holds fully 10 c.c., and is graduated to 0.1 c.c. Twenty c.c. of a recently-prepared 30% sodium hydrogen sulphite solution are added, and the mass shaken until solidified. After fifteen minutes, the flask is suspended in a water-bath at 85°, and, when with constant shaking the mass has liquefied, the flask is three-fourths filled with the sulphite solution. After four to six minutes, a layer of oil will have formed, and more of the reagent is then added until the flask is filled up to the neck. After eight minutes, more is added so as to fill the graduated neck, and, after keeping the flask in the water-bath for another ten minutes, it is taken out and allowed to cool. The volume of unabsorbed oil is then read off.

L. DE K.

Titration of Chloral Hydrate. JULES GARNIER (*Chem. Zentr.*, 1908, i, 1492; from *Bull. Sci. Pharmacol.*, 1908, 15, 77—82).—In order to prevent a secondary reaction from taking place between the chloroform formed and the alkali, the test should be carried out as follows: 0.1655 gram of the sample is dissolved in 10 c.c. of water, and 12.5 c.c. of *N* 10 potassium hydroxide are added. The temperature should not exceed 15°, and, after fifteen to twenty minutes, the excess of alkali is titrated with *N* 10 sulphuric acid, with phenolphthalein as indicator. Another experiment should then be made, using only the slightest excess of alkali.

L. DE K.

Estimation of Acetone in Urine. T. STUART HART (*J. Biol. Chem.*, 1908, 4, 477—482).—The acetoacetic acid in the urine is first converted into acetone by heating at 100° ; the acetone is then drawn by a current of air into the absorbing cylinder, as in Folin's method (Abstr., 1907, ii, 588). The values for total acetone plus acetoacetic acid closely approximate to those obtained by the more lengthy Messinger-Huppert procedure. W. D. H.

The Estimation of Indole in Fæces by Herter and Foster's Method. E. GORTER and W. C. DE GRAAFF (*Pharm. Weekblad*, 1908, 45, 842—845).—Fæces are distilled with steam in presence of potassium hydroxide, and the distillate again distilled with steam after acidification with sulphuric acid. The indole is estimated in the second distillate by Herter and Foster's colorimetric method, using a standard solution prepared from pure indole. A. J. W.

Direct Application of Kerner's and of Liebig-Hesse's Process to Quinine Disulphate. PIETRO BIGINELLI (*Chem. Zentr.*, 1908, i, 1499—1500; from *Mon. Sci.*, 1908, [iv], 22, 185—187).—The conversion of the quinine disulphate into the normal salt is effected in the cold by lead carbonate (also compare Abstr., 1907, ii, 317). L. DE K.

Estimation of Casein: Determination of its Molecular Weight. GEORGE TH. MATTHAIPOULOS (*Zeitsch. anal. Chem.*, 1908, 47, 492—501).—The process is based on the fact that casein forms a definite compound with sodium hydroxide when using phenolphthalein as indicator; in this compound, the casein seems to have a molecular weight of 1131.5, practically agreeing with the molecular weight 1135 attributed to it by Laqueur and Sackur (Abstr., 1903, i, 300).

The analysis is conducted as follows: In two separate beakers are placed 80 c.c. of water and 20 c.c. of milk, $N/25$ sulphuric acid is added to the milk until the casein appears to be completely precipitated, and the same amount is then added to the second beaker; as a rule, some 21 c.c. are required. To the contents of the control beaker is now added 1 c.c. of 1% alcoholic phenolphthalein, and the whole titrated with $N/10$ sodium hydroxide. The contents of the other beaker are filtered until 100 c.c. of a clear filtrate have been obtained. This is then also titrated with $N/10$ soda, and, after making allowance for the dilution caused by the acid added, the difference in the titrations represents the alkali absorbed by the casein; 1 c.c. of $N/10$ alkali = 0.11315 gram of casein. L. DE K.

Pettenkoffer's Reaction. GABRIEL GUÉRIN (*J. Pharm. Chim.*, 1908, vi], 28, 54—54).—The Pettenkoffer reaction for biliary acids is due to the formation of a trace of furfuraldehyde from the sugar added, and, in fact, a trace of this aldehyde may be substituted for the sugar.

The author now states that if a larger quantity of furfuraldehyde is employed, the colour generated is not purple, but blue. The test may be applied as follows: A small quantity of the biliary salts is dissolved in 1—2 c.c. of alcohol, 5—6 drops of a saturated aqueous solution of

furfuraldehyde are added, and then slowly an equal volume of sulphuric acid, when the blue colour will be developed at once. If an aqueous solution has to be tested, twice the quantity of furfuraldehyde should be employed.

The blue coloration is due entirely to the formation of cholic acid.

L. DE K.

Colour Test for Aल्पine and various other Local Anæsthetics. P. LEMAIRE (*Ann. Chim. anal.*, 1908, 13, 301—303).—The author has successfully applied the sulphonation test for benzoic acid to some local anæsthetics.

Two c.c. of pure sulphuric acid are placed in a test-tube, 0.05 gram of the substance is added, and the mixture heated until white fumes appear. 0.4 Gram of potassium nitrate in fine crystals is then added in small portions, and, when cold, the liquid is poured carefully into a beaker containing 25 c.c. of dilute ammonia (1:1). On adding a drop of ammonium hydrogen sulphide, a reddish brown coloration appears. The test is successful with aल्पine (benzoyltetramethyl- β -aminopentanol hydrochloride), stovaine (benzoyldimethylaminopentanol hydrochloride), cocaine hydrochloride, tropacocaine hydrochloride, α -eucaine hydrochloride, and β -eucaine hydrochloride.

With other substances of this class, the test is indistinct, owing to secondary reactions.

L. DE K.

General and Physical Chemistry.

Refraction and Dispersion of Helium. KURT HERRMANN (*Ber. deut. physikal. Ges.*, 1908, 8, 476—482. Compare this vol., ii, 333).—Measurements of the refraction of air, hydrogen, and helium have been made for the cadmium line $\lambda = 0.6438\mu$. The values of the refractive index are for air 1.0002930, hydrogen 1.0001380, helium 1.00003406, at 0° and 760 mm. The values of v in the expression for the relative dispersion $1/v = (n_F - n_C)/(n_D - 1)$, where n_F , n_C , and n_D are the refractive indices for the lines F , C , and D , are for air 98.0, hydrogen 65.9, and helium 39.9. H. M. D.

Index of Refraction of Mixtures of Alcohols and Water. II. ANTONY G. DOROSCHEWSKY and S. V. DVORSCHANSCHIK (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 908—931. Compare this vol., ii, 241).—The curves connecting the index of refraction of aqueous alcohol with the proportion of alcohol present for thallium, lithium, and sodium lights are of the same type, all exhibiting maxima at the same concentration; the curves become less convex as the wave-length is increased. Rise of temperature also results in a flattening of the curve, and in a displacement of the position of the maximum towards the water axis.

When water is added to isopropyl alcohol, a well-defined maximum refrangibility, corresponding with 93—94% of the alcohol, is observed. With normal propyl alcohol, a less clearly marked maximum exists at about 97%. With butyl and isobutyl alcohols, addition of water causes lowering of the index of refraction, no maximum being observed. The rate of change of the index of refraction with temperature, dn/dt , also varies regularly, exhibiting a maximum in the region of the maximum index of refraction. In general, the magnitude of dn/dt for propyl, isopropyl, butyl, and isobutyl alcohols varies little, but diminishes slightly as the molecular weight of the alcohol increases, and is greater for the isovalcohols than for the normal ones.

The value of a in Pulfrich's formula (*Zeitsch. physikal. Chem.*, 1889, 4, 561) $(n - n_0)/n = a(D - D_0)/D$ has been calculated for mixtures of ethyl, propyl, and isopropyl alcohols with water, and is found to be a constant independent of the temperature and of the wave-length of the light used. For ethyl alcohol, the mean value of a is 0.975, for propyl alcohol, 0.92, and for isopropyl alcohol, 0.95. Knowing the value of a , the indices of refraction of mixtures of alcohol and water, and the specific gravities and indices of refraction of absolute alcohol and water, the composition of the aqueous alcoholic mixtures can be calculated; results obtained in this way for various mixtures of ethyl alcohol and water at 15°, 20°, and 30° agree closely with the experimental numbers. Calculation of the concentration of mixtures of alcohol and water by means of Gladstone's formula, $(n - 1)/d = \text{const.}$,

yields accurate results, which are also given by Pulfrich's (*loc. cit.*) modification of Gladstone's formula.

The expansion of liquids by heat is expressed with great accuracy by the equation $v_t = v_0/(1 - kt)$ (compare Mendelëff, *J. Russ. Phys. Chem. Soc.*, 1884, 18, 1). The authors find that a similar equation, $n_t = n_0/(1 + kt)$, gives accurately the relation between the index of refraction of a liquid and the temperature; k is termed the modulus of the index of refraction.

T. H. P.

New Law of Series Spectra. W. RITZ (*Physikal. Zeitsch.*, 1908, 9, 521—529).—A formula is given by means of which new series of spectral lines can be deduced from known series. The newly-discovered series of lines in the spectra of the alkali metals are accurately represented by means of the formula, and it is also shown that the series of lines in the spectra of helium, copper, and the alkaline earth metals are in agreement with it.

H. M. D.

Spectrum of the Lighter Constituents of Air. HERBERT E. WATSON (*Proc. Roy. Soc.*, 1908, 81, A, 181—194).—The lighter portions of air were separated by fractional distillation by Coates (*Abstr.*, 1907, ii, 237), and the portion not absorbed by charcoal at -140° was further fractionated. One fraction pumped off charcoal at -205° , and a second fraction at -190° , have now been examined spectroscopically by the author. The spectra of the first order, and, for all lines of wave-length less than 4100, of the second order as well, obtained with a Rowland grating, were photographed. A very long exposure was given in order that faint lines might not be overlooked.

The wave-lengths obtained, along with those of Living and Dewar (*Abstr.*, 1904, ii, 213) and Baly (*Abstr.*, 1904, ii, 3) for comparison, are given in tabular form. After allowing for the lines ordinarily ascribed to helium and neon (and also to traces of argon and hydrogen), a considerable number of lines remain unaccounted for. These lines, however, do not appear to show more than accidental coincidences with any of the chief nebular or coronal lines, or with any of the lines of the spectrum of the solar chromosphere. It seems probable, therefore, that the majority are really neon lines which were not observed previously owing to insufficient exposure, and there is no evidence that the fractions contain gases other than those already mentioned.

G. S.

Spectrum of Radium Emanation. ALEXANDER T. CAMERON and SIR WILLIAM RAMSAY (*Proc. Roy. Soc.*, 1908, 81, A, 210—213).—In a previous paper (*Abstr.*, 1904, ii, 529), Ramsay and Collie gave measurements of the spectrum of radium emanation obtained with a direct vision spectroscope. The spectrum in question has now been photographed. Three successive photographs were taken, but only the first showed the spectrum of the emanation alone, as the effect of the discharge is to drive the emanation towards the negative electrode, where it is largely absorbed, and the tube soon shows only the hydrogen spectrum.

Much better results were obtained with copper electrodes in place of the aluminium electrodes first used. The former electrodes appear not to contain hydrogen, and absorb the emanation much more slowly than aluminium does.

The wave-lengths and intensities of the lines ascribed to the emanation are given in the paper (compare Rutherford and Roys, following abstract). G. S.

Spectrum of Radium Emanation. ERNEST RUTHERFORD and T. ROYS (*Phil. Mag.*, 1908, [vi], 16, 313—317. Compare Cameron and Ramsay, preceding abstract).—The spectrum of radium emanation purified as well as possible from permanent gases and carbon dioxide was found to consist of entirely characteristic lines. The authors have mapped a spectrum of seventy-four lines between 3612.2 \AA and 6079 \AA , thirty-nine lines being observed visually, and sixty-three photographed. None of these lines has been identified in any stellar spectrum. The colour of the discharge is bluish, the spectrum being characterised by groups of brilliant green and violet lines.

During the passage of the discharge, the emanation lines grow gradually weaker, and the emanation itself appears to be driven into the walls of the tube, whence it is removed with difficulty by strongly heating the glass. After three days, the glass is much blackened, and the principal lines of helium appear in the spectrum. R. J. C.

Quantitative Indications Furnished by Dissociation Spectra: Silver. ANTOINE DE GRAMONT (*Compt. rend.*, 1908, 147, 307—309. Compare Abstr., 1907, ii, 728; this vol., ii, 645).—The following series of argentiferous materials have been examined spectroscopically, employing the simple or oscillating condensed spark: (1) galena; (2) commercial lead; (3) alloys of lead and silver; (4) alloys of tin and silver, all of known composition. Spectra of the four classes have been photographed on the same plate, and to render the quantitative indications comparable, six spectra of each class, representing six different concentrations of silver, have been recorded by vertical movement of the plate. It is found that the number and intensity of the lines for silver have a direct and constant relation to the concentration of the metal in the sample. A table is given showing the lines which disappear at different concentrations of silver from 1% to 0.0001%.

It is necessary to guard against certain foreign lines which coincide with those of silver, and also against the halo occasioned by bright lines of lead or tin. W. O. W.

Apparatus for Producing Coloured Flames. ROBERT GOLDMANT (*Bull. Soc. chim. Belg.*, 1908, 22, 255—259).—A description and sketch of a simple arrangement for obtaining a flame permanently and intensely coloured.

The air supply of a Bunsen flame is charged with a spray produced by electrolysis of a suitable solution. W. O. W.

Electro-optical Properties of Liquid Mixtures. J. CHAUDIER (*Ann. Chim. Phys.*, 1908, [viii], 15, 67—140).—The author first gives a résumé of previous work on the changes undergone by light when it traverses a liquid situated in a magnetic field (compare Majorana, *Atti. R. Accad. Lincei*, 1903, 11, i, 374, 463, 531; 11, ii, 90, 139; Meslin, *Abstr.*, 1903, ii, 408, 521, 585).

The laws of electric dichroism are shown, theoretically and experimentally, to be similar to those established by Meslin (*loc. cit.*) for magnetic dichroism. But whilst the sign of electric dichroism is independent of the relative value of the dielectric constants of the media, that of magnetic dichroism can be altered by modifying the relative value of the magnetic constants of the solid and surrounding liquid. The dichroism is proportional to the length of liquid traversed by the light and to the concentration of the liquid, and increases with the intensity of the field to a limiting value.

A mixture of liquids placed in a uniform electric field exhibits marked birefractation, provided that the suspended particles are sufficiently minute.

The field due to gravity is also capable of producing the phenomena of dichroism and even of birefractation. The action of any uniform field is hence manifested in an orientation of the particles of mixed active liquids, which then exhibit the phenomena of dichroism and birefractation; the laws of these phenomena are the same whatever the nature of the field, provided that account is taken of the change of sign due to diamagnetism. If the particles in suspension have a greater magnitude than about 0.3 mm., dichroism alone is observed, and is due to the reflection of light by the crystalline surfaces. If the particles are smaller and uniform in size, dichroism is still the principal phenomenon observed, but birefractation also appears, and the modifications due to diffraction come into play. As the dimensions of the particles diminish, dichroism becomes rarer, and birefractation plays a more important rôle, whilst, when they are infinitely small, as in colloidal solutions, the phenomena of reflection and refraction are no longer produced and the liquids are only birefractive. T. H. P.

Electrochemistry of Light. III. Halogen Carriers. WILDER D. BANCROFT (*J. Physical Chem.*, 1908, 12, 417—447. Compare this vol., ii, 448, 549).—The facts and theories relating to the action of carriers in the chlorination and bromination of hydrocarbons are discussed, and a new theory is put forward which resembles in some respects that advanced by Briner (this vol., i, 146).

The chief conclusions at which the author arrives are that the action of halogen carriers is not due to the intermediate formation of additive compounds, and that under suitable conditions the carriers react with the hydrocarbons even in the absence of free halogen.

To account for the observed facts of substitution in the side-chain and in the nucleus, it is supposed that the halogens and the carriers give rise to ions, and that substitution takes place in the nucleus when the negative ions are present in excess and in the side-chain when the positive ions predominate. By means of this theory, the catalytic action of ferric, stannic, and aluminium chlorides, as well as of iodine

monochloride, phosphorus pentachloride, water, and sunlight, can be accounted for. The facts relating to the velocity of the reactions when certain of these carriers are employed can also be explained.

H. M. D.

Photographic Action of Metals and Hydrogen Peroxide (So-called Metallic Radiation). SEM SÄRLAND (*Ann. Physik*, 1908, [iv], 26, 899—917. Compare Russell, *Abstr.*, 1898, ii, 287; 1899, ii, 720).—An investigation has been made of the conditions under which photographic action is produced by certain metals and by solutions of hydrogen peroxide, and from the results the author concludes that the action of the metals is due to chemical changes and not to the emission of any special type of radiation.

The activity of the metals, measured immediately after polishing the surface, increases with the electropositive character, and the greater the activity of the freshly-polished metal the more rapidly does this activity diminish with time. When the metal is kept in a vacuum, this diminution in the activity does not take place. The photographic activity is also unaltered after the metals have been heated, and exposure to an electrical field has no influence on the photographic effect. The darkening of the plates is greatly increased if the plates are left undeveloped for some time, or if before developing they are gently heated.

In a vacuum containing phosphoric oxide, the photographic action does not take place; conditions under which hydrogen peroxide can be formed appear to be essential. Experiments are also described which indicate that the action does not spread from the active metals in a rectilinear manner, but that, on the other hand, the distribution is such as would be expected if gaseous diffusion were taking place. The photographic action is not observed when certain metals, such as copper, or alloys, like brass, are interposed as diaphragms between the active metals and the photographic plate. It is also inhibited if very thin, non-porous sheets of metals are interposed, or if a sufficiently rapid current of air is passed between the photographic plate and the active metal.

The observations indicate the identity of the action of metals and of hydrogen peroxide solutions. The metals therefore exhibit photographic activity in consequence of the formation of hydrogen peroxide, and are only active when the conditions are such that hydrogen peroxide can be produced.

H. M. D.

Relation of Absorption and Sensitiveness in Photographic Preparations. ERICH LEHMANN (*Zeitsch. physikal. Chem.*, 1908, 64, 99—119).—The question as to the influence of wave-length on the relation of optical absorption to photochemical extinction has not hitherto received a definite answer. The author shows that in the case of silver iodide a solution of the problem is possible. For silver iodide either by itself or in collodion, the maximum of absorption and the maximum of sensitiveness are coincident. In a gelatin emulsion of silver iodide, however, the maximum of sensitiveness is displaced

16.65 μ relatively to the absorption maximum. This may be due to the formation of an organic silver salt.

It is exceedingly probable that similar results would be obtained with silver chloride and bromide if these substances could be subjected to direct observation.

J. C. P.

Photochemical Oxidation of Hydrogen Iodide by Oxygen. JOH. PLOTNIKOFF (*Zeitsch. physikal. Chem.*, 1908, 64, 215—228. Compare Abstr., 1907, ii, 212).—The rate of decrease of the oxygen concentration is now found to be proportional to the 2/3 power of the acid concentration both in the light and in the dark. The fact that in the earlier work different values were found for the exponent of the hydrochloric acid concentration in the light and in the dark was probably due to some catalytic agent, and it is now shown that the presence of copper sulphate is sufficient to cause such a difference.

For the reaction in the dark, the value of K_{T+10}/K_T is now found to be 2.07; for the reaction in the light the value is 1.38.

The author's further experiments show that the photochemical oxidation of hydrogen iodide by oxygen is the sum of two independent changes: (1) the reaction in the dark; (2) the reaction in the light. Hence the velocity may be represented by the formula: $-d(O_2)/dt = [K_1 \cdot 10^{aT} + K_2 \cdot I \cdot 10^{bT}](HCl)^2(KI)^2(O_2)$.

J. C. P.

Method of Carbon Dioxide Assimilation. EMIL BAUR (*Zeitsch. physikal. Chem.*, 1908, 63, 683—710).—A solution of potassium ferric oxalate in diffused daylight evolves carbon dioxide, but the evolution of gas ceases before all the ferric salt is decomposed. When a solution of potassium ferrous oxalate is kept in an atmosphere of carbon dioxide, the gas is gradually absorbed, and ferric salt is produced. These observations may be summed up in the equation: $Fe(C_2O_4)_3K_3 = Fe(C_2O_4)_2K_2 + \frac{1}{2}C_2O_4K_2 + CO_2$.

The reversibility of this reaction has led the author to consider the suggestion, that in the original production of organic compounds the reduction of carbon dioxide to oxalic acid was the first stage. In order to make the energy of light available for this reduction, the system ferrous oxalate + ferric oxalate + carbon dioxide must be combined with a system in which oxygen is developed under the influence of light. This latter result is attained, for instance, when silver chloride immersed in water is exposed to light, and the author shows how in a vessel provided with a septum of photochloride and a semipermeable membrane it would be possible, theoretically at least, to effect the conversion of carbon dioxide and water into oxalic acid and oxygen. In endeavouring to find other systems which, like silver chloride in water, would evolve oxygen on exposure to light, the author has studied the way in which the potentials of iron, mercury, uranium, and cerium salts are affected by light. The P.D. at a platinum electrode immersed in a solution containing both uranous and uranyl salts is actually less positive when exposed to sunlight than when kept in the dark. The displacement of potential is considerable, and takes place more or less rapidly according to the

nature of the salts employed. The results obtained with iron, mercury, and cerium salts were less noteworthy.

The term "light content" ("Lichtinhalt") is proposed for the quantity of energy which is absorbed by a light-sensitive substance, and which goes to change its chemical potential. The value of this "light content" is deduced from the *E.M.F.* of photoelectric cells and their temperature-coefficients.

J. C. P.

Distribution of the Radiation from Radioactive Substances. HEINRICH W. SCHMIDT (*Physikal. Zeitsch.*, 1908, 9, 537-541).—To explain the irregular distribution of the radiation from substances containing uranium, which Greinacher (this vol., ii, 551) found on examination of photographic plates which had been placed in contact with these substances cut into sections of well-defined geometrical forms, it is not necessary to attribute the action to secondary rays. The phenomenon can be referred to the action of the β -rays if it is assumed that the emitted rays follow the cosine law of Lambert. Conversely, the experimental observations indicate the validity of this law in the case of corpuscular radiation.

H. M. D.

Experiments with Radium Emanation. VOLUME OF THE EMANATION. ERNEST RUTHERFORD (*Phil. Mag.*, 1908, 16, 300-312).—The amount of emanation in equilibrium with one gram of radium is $q\lambda$, where q is the rate of production per second and λ is the radioactive constant of the emanation. The value of λ is about $1/468000$.

Assuming that one atom of radium emits one α -particle and then becomes one atom of emanation, and knowing the number of α -particles emitted per second and the charge on each (Rutherford and Geiger, this vol., ii, 794), the author calculates the volume of the emanation to be 0.57 cub. mm. per gram of radium. Ramsay and Cameron, however (*Trans.*, 1907, 91, 1266), obtained 7.07 cub. mm. of emanation from one gram of radium. The author finds that probably 80% of the gas measured by these authors consisted of matter foreign to the emanation itself.

To obtain pure emanation, radium bromide was either heated in a quartz tube or dissolved in water, the emanation being pumped off with the oxygen and hydrogen formed, and sparked down as described by Ramsay. The emanation was collected over potassium hydroxide, and condensed by cooling in liquid air. After all uncondensed gases had been pumped off, the emanation was allowed to gasify and remain some hours in contact with potassium hydroxide. It was finally liquefied again by liquid pentane at a temperature between 150° and 186° and exhausted by the pump, a portion being volatilised and lost in the process. Difficulty was experienced in obtaining the emanation free from carbon dioxide, although phosphoric oxide was used to lubricate the stopcocks and the emanation frequently stood twenty-four hours over potassium hydroxide. The emanation, as finally measured in a capillary tube, was in such a state of purity that the spectrum of carbon dioxide was hardly seen, but a new spectrum of bright lines certainly due to the emanation itself appeared.

The amount of radium corresponding with the amount of emanation measured was estimated by comparing the γ -ray activity of the emanation with that of a standard sample of radium bromide. When the emanation was well purified, its volume varied from 0.80 to 1.32 cub. mm. per gram of radium, decreasing rapidly and spontaneously to 0.58 to 0.66 cub. mm. The average final volume corrected for temperature and pressure was 0.58 cub. mm. The highly-purified emanation had the usual half-period of 3.75 days, and the author finds it difficult to explain the spontaneous contraction. In one experiment when purified emanation was left eleven days in the capillary, its volume greatly increased again, and a brilliant spectrum was obtained showing all the lines of helium. Passage of electric sparks caused the emanation to condense on the glass walls of the capillary, leaving only carbon dioxide. At the temperature of liquid air, the emanation has a sensible vapour pressure.

R. J. C.

Relative Activity of Emanation and Active Deposit from Thorium and from Actinium. HOWARD L. BRONSON (*Phil. Mag.*, 1908, [vi], 16, 291—299).—It is frequently assumed that each atom of the various radioactive substances gives off either one or no α -particle each time it undergoes transformation. The author's comparisons of the relative activity of emanation and active deposit in the cases of thorium and actinium, making due allowance for the different mean free paths of the α -particles in the various cases, fail to support this view.

A quantity of the volatile radioactive products from thorium or actinium was conveyed to the testing vessel by a current of air, and its total ionising activity was measured. After waiting a short time to allow the emanation to decay, the residual ionising activity due to the active deposit was measured. The activity of the emanation was obtained by difference. Knowing the rates of transformation of all the products, the activity of the deposit when at its maximum value could be calculated.

The ratio of ionisation due to active deposit to that due to emanation was found to vary from 0.34 to 0.40 in the case of thorium, and from 0.28 to 0.41 with actinium, different ratios being obtained with measuring vessels of different sizes.

The active deposit from thorium is supposed to contain thorium *B* and thorium *C*. In all cases with thorium, the calculated ionisation ratio was four times as great as the measured ratio, whilst with actinium the calculated ratio was always twice as great as the measured. The presence of other substances of short transformation periods would serve to explain the results, but there is no evidence for this (compare Hahn, *Abstr.*, 1906, ii, 718). The author prefers to suppose that atoms of thorium *B* and thorium *C* give off the same number of α -particles during transformation, but that an atom of thorium emanation gives off four times as many; also, that a disintegrating atom of actinium emanation gives off twice as many α -particles as an atom of its active deposit. On the other hand, radium emanation, radium *A*, and radium *C* appear to give off the same number of α -particles per atom. The actual number of ejected

α -particles per atom cannot be stated as the determinations are only relative.

R. J. C.

Ozonisation of Air by the Action of Radium Salts and Emanation. RAFFAELLO NASINI and MARIO G. LEVI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 46—49).—The authors discuss the formation of ozone by radium salts, which is affirmed by Madame Curie and by Giesel, but denied by Ramsay and by Soddy. The authors' experiments show that, in presence of a large excess of air or oxygen, ozone is formed by the action of radium.

A small bottle containing 0.005 gram of radium bromide dissolved in 30 c.c. of water was placed open in a 5-litre flask containing air. When the flask was closed by a ground-glass stopper, after some hours the air inside gave the reactions of ozone, but if a cork or a rubber stopper was used, the air gave no odour or reactions of ozone, which had been destroyed.

Further experiments indicate that the emanation itself cannot produce ozone, but the results cannot be regarded as absolutely decisive.

T. H. P.

Action of Radium Emanation on Solutions of Copper Salts. MADAME MARIE CURIE and Mlle. GLEDITSCH (*Compt. rend.*, 1908, 147, 345—349).—The authors have repeated Cameron and Ramsay's experiments (*Trans.*, 1907, 91, 1593) on the action of radium emanation on copper salts, taking special precautions to employ apparatus and reagents free from traces of lithium. Platinum vessels were used, since it was found that distilled water free from lithium becomes contaminated with traces of this element when allowed to remain in contact with glass for twenty-four hours. The use of quartz vessels, especially of the transparent variety, is inadmissible, since these contain notable amounts of lithium. The water and acids necessary were distilled in platinum retorts, and the reagents were not allowed to come into contact with glass during the experiments. It was found practically impossible to remove the last traces of lithium from copper sulphate. After allowing the emanation to act on the solution, the copper was removed, and, after evaporation of the liquid, the residue, which weighed about 0.0004 gram, was examined spectroscopically. Sodium and potassium were found to be present, but lithium could not be detected. Comparative experiments on sodium sulphate containing known quantities of lithium sulphate indicated that the residue could not have contained more than 0.6×10^{-5} milligram lithium. In order to show that no lithium was lost during the experiment, a control experiment was carried out on a solution containing 0.27 gram of copper and an amount of lithium sulphate equivalent to 1.7×10^{-4} milligram of the chloride. After removal of the copper, lithium was readily detected in the residue.

The authors consider that the formation of sodium and lithium has not been established by Cameron and Ramsay.

W. O. W.

Retardation of α -Rays by Metal Foils, and its Variation with the Speed of the α -Particles. T. SMITH TAYLOR (*Amer. J. Sci.*, 1908, [iv], 26, 169—179).—In the experiments of Bragg and

Kleeman, and also in those of Kučera and Mašek (Abstr., 1907, ii, 4), McClung (Abstr., 1906, ii, 138), Rutherford (Abstr., 1906, ii, 612), and Levin (Abstr., 1906, ii, 595), on the effect produced on the range of α -particles by the interposition of sheets of metals, the air equivalents corresponding with different positions of the screen were obtained by determining the difference of the range with the source of the rays uncovered and with the screen in place. As this method is not very accurate, a new method has been devised, and is described in the present paper.

Polonium was used as the source of the rays, and experiments were made with thin sheets of gold, lead, tin, aluminium, and silver of varying thickness. The results show that the air equivalents of sheets of metal foil decrease with the range, and hence with the speed, of the α -particles. The change is very small for thin foil of the lighter metals when the range of the α -particles is high, but for thicker sheets or a lower range, the change is more considerable. A comparison of the change for sheets of different metals of nearly equal air equivalents shows that the rate of change is in the order of the atomic weights of the metals.

E. G.

Charge and Nature of the α -Particle. ERNEST RUTHERFORD and HANS GEIGER (*Proc. Roy. Soc.*, 1908, 81, A, 162—173. Compare this vol., ii, 555).—The total charge carried by the α -particles expelled per second from a known weight of radium has been determined directly, and from the result and the number of α -particles expelled per second per gram of radium, the charge carried by an α -particle has been calculated as 9.3×10^{-19} E.S. units. In determining the total charge carried by the particles, radium C was used as a source of radiation; the particles passed through aluminium plates into a testing chamber, and the current was measured in the usual way. The methods used to eliminate other rays, and to determine the strength of the radiating source, are fully described.

The charge carried by an α -particle, calculated on the assumption that the heating effect of radium is a measure of the kinetic energy of the α -particles expelled from it, is 9.1×10^{-19} E.S. units, in good agreement with the above value. The charge e carried by a hydrogen atom has been estimated by J. J. Thomson, H. A. Wilson, and others at $3\text{--}4 \times 10^{-19}$ E.S. units, from which it would follow that the charge on the α -particle is between $2e$ and $3e$. Reasons are given for the assumption that the values hitherto found for e are too low. As the α -particle probably carries $2e$, the most probable value for e is 4.65×10^{-19} E.S. units. Support is lent to this view by a new calculation of e from the known period of transformation of radium, the result obtained being 4.1×10^{-19} E.S. units.

As the ratio of the charge on the α -particle to its mass has already been determined, the mass (atomic weight) of the α -particle has now been calculated as 3.84, which supports Rutherford's previous suggestion that the α -particle, after it has lost its positive charge, is a helium atom.

From the data now available, some important radioactive magnitudes, such as the volume of the emanation and the rate of production of helium, have been calculated.

(G.S.)

Scattering of the α -Particles by Matter. HANS GEIGER (*Proc. Roy. Soc.*, 1908, 81, 4, 174—177).—Radium emanation was employed as a source of α -particles; these were allowed to pass through a narrow slit on their way to a phosphorescent screen, and from a comparison of the area reached by the rays (as determined by observing the scintillations) with the magnitude of the geometrical image of the slit, the amount of scattering could be ascertained.

In a vacuum, scarcely any scintillations were observed outside the image of the slit, but, when air was allowed to enter, the area of scintillation increased. The same effect was produced in a vacuum when the slit was covered with gold leaf, and to a smaller extent when aluminium foil was employed.

G. S.

Secondary γ -Rays due to γ -Rays of Radium C. A. S. EVE (*Phil. Mag.*, 1908, [vi], 16, 224—234).—The intensity of secondary cathode radiation from various substances under the impact of Röntgen rays, β -rays, and γ -rays has been shown to be a function of the atomic weight of the secondary radiator, but comparison of Townsend's determinations of secondary radiation, from various substances under the influence of X-rays, with the author's values for the total secondary radiation produced by γ -rays, reveals striking discrepancies. The author has endeavoured to find the origin of these differences, which, if Röntgen rays and γ -rays are fundamentally of the same nature, ought not to arise.

Upwards of 30% of the secondary radiation may consist of secondary γ -rays with a penetrating power equal to that of primary γ -rays from actinium, but greater than that of primary γ -rays from uranium or radium. One or two millimetres of lead or aluminium suffice to absorb completely the secondary cathode rays from lead, iron, or brick radiators, but allow the secondary γ -rays to pass. When comparative experiments are made in such a way that cathode secondary rays are absorbed and only secondary γ -rays reach the electro-scope, the secondary effects produced by X-rays and γ -rays of radium are neither in order of the atomic weights nor of the densities of the radiators, and are not in agreement with one another. The secondary rays which reach the electro-scope are γ -rays, and not penetrating cathode rays, since their intensity is not affected by a strong magnetic field.

The differences apparently lie more in the velocity than in the nature of the particles. Even cathode secondary radiation, which follows the order of the atomic weights, has a much higher velocity when excited by β - or γ -rays than by X-rays. The similarity of the β - and γ -ray effects in this instance is held to support Bragg's theory that β - and γ -particles are essentially the same, but bear different charges.

The intensity of the secondary γ -rays induced by primary γ -rays from radium depends on the material surrounding the radium. Primary γ -rays traverse steel more readily than lead, but rays which have passed through steel are more readily absorbed by lead than rays which have already passed through lead. Taking the case of radium enclosed in a glass tube, the secondary radiation due to γ -radiation is 7.5% of that due to β - and γ -radiation together. Of this 7.5%, the

larger part is cathode secondary radiation, the proportion of γ -radiation in it being 6.2% from lead, 25% from iron, and 28% from brick.

The coefficient of absorption of primary γ -rays from radium is 0.45—0.57, from uranium 1.4, from actinium 2.7—4.7, whilst the secondary γ -rays excited by radium γ -rays in lead, iron, and brick have a coefficient about 4.6. The author is of the opinion that secondary γ -rays caused by the primary γ -rays of actinium would have a coefficient of absorption even lower than 4.6, and approximating to that of X-rays.

R. J. C.

Polonium Rays. CH. LATRÈS (*Chem. Zentr.*, 1908, i, 2137—2138; from *Le Radium*, 1908, 5, 97—102).—The author has endeavoured to obtain evidence of the production of secondary rays when polonium rays fall upon a metal plate by means of delicate electrical and photographic processes. In this he has been unsuccessful, although it is probable that secondary rays are produced (Logeman, *Abstr.*, 1906, ii, 721), and should be photographically detectable.

J. V. E.

Radioactivity of Certain Goitrogenic Springs. RÉPAX (*Compt. rend.*, 1908, 147, 387—388).—Three samples of spring water from the neighbourhood of St. Jean de Maurienne were found to be distinctly radioactive ($A=0.011$ to 0.031 in Curie-Laborde units). Endemic goitre is known to be prevalent in the districts where these waters are used for drinking purposes, and the author suggests that the well-known disappearance of goitrogenic properties which takes place after the lapse of time is connected with the decay in the radioactivity of the waters.

W. O. W.

Invisible Radiations from the Explosive Discharge in Air. I. SCHISCAGLIA (*Nuovo Cim.*, 1908, [v], 15, 481—491).—An apparatus is described which allows of the very accurate regulation of a spark gap, in order to study the effect of radiations from another spark in causing the spark to pass. The transparency of various liquids to the invisible rays was examined by enclosing them in a quartz or selenite cell and interposing them between the spark gaps.

Whilst water and alcohol are transparent, metallic salts and many organic liquids, such as turpentine, carbon disulphide, and petroleum, are highly opaque, indicating that the radiation from the spark does not contain extreme ultra-violet rays.

C. H. D.

Radiation from Drying Oils. WERNER SCHMIDT (*Zeitsch. physikal. Chem.*, 1908, 64, 243—250).—Gum arabic when kept in the neighbourhood of linseed-oil varnish is found to undergo a slow change and becomes insoluble. If a gum solution contains a little chromate, the gum is rendered insoluble, rapidly when exposed to light, and more slowly when exposed to linseed-oil varnish in a dark room. This analogy between the action of light and the action of the drying oil is borne out by a study of the effect of the latter on a photographic plate. The radiation from the oil affects the plate even through

of gelatin or paper, and if a perforated sheet of metal is interposed, an image is obtained. The phenomenon of solarisation has also been observed.

This behaviour of linseed-oil varnish is connected with the oxidation which goes on during drying, and which is possibly accompanied by the formation of ozone or other compounds of a superoxide character. It has been noticed that the bright surface of a metal plate exposed in the neighbourhood of a linseed-oil varnish shows evidence of oxidation.

J. C. P.

Formation of Mists in Presence of Radium Emanation.
MADAME MARIE CURIE (*Compt. rend.*, 1908, 147, 379—382. Compare this vol., ii, 7).—The appearance of mists in moist gases induced by radium emanation appears to be due to the formation in the gases of chemical compounds capable of absorbing water vapour. The gases experimented on were contained in sealed glass bulbs illuminated by the electric arc. Air containing pure water vapour and charged with emanation gives a slight mist, persisting for several days; a mist is not produced when the air is replaced by carbon dioxide. If the water contains half its weight of sulphuric acid, an intense mist, lasting for several months, is produced whether the gas employed is air or carbon dioxide.

A permanent mist is also obtained in a bulb containing concentrated sulphuric acid and carbon dioxide; in a blank experiment without emanation, a still more intense mist was produced on warming the bulb, but this disappeared in less than a day. When caoutchouc stoppers are used to close the bulbs, the mists are very dense and persistent, probably through the oxidation of sulphur and organic matter giving rise to products capable of acting as centres of condensation. This is confirmed by the production of a fine, persistent mist in a bulb containing water, air, and emanation, with a fragment of sulphur kept out of contact with the water; at the end of the experiment, sulphuric acid is present in the water. The presence of nitric acid has also been detected when air has been used.

Similar mists are formed in air charged with light petroleum or carbon disulphide, and also in carbon dioxide containing anhydrous ether with emanation. In some instances, mists are formed when solids are employed; in these cases, a deposit is visible on the sides of the vessel. Emanation induces a mist in carbon dioxide containing iodine, or in air containing camphor; in the first instance, the mist subsides in a few days. Actinium causes a mist in moist carbon dioxide.

The drops constituting the mist in the foregoing experiments behave as if they had no electrostatic charge when introduced into an electric field.

W. O. W.

Supersaturation and Nuclear Condensation of Certain Organic Vapours. T. H. LADY (*Phil. Trans.*, 1908, A, 208, 445, 474; *Proc. Roy. Soc.*, 1908, 81, A, 219—220).—Dust-free air, saturated with an organic vapour (ester, acid, or alcohol), was subjected to sudden adiabatic expansion in a special apparatus, and the least expansion required to produce condensation of the vapour noted. The

effect of the presence of ionic nuclei, obtained by previous exposure to Röntgen rays, on the conditions of condensation was also noted, as well as the different effects produced according as positive or negative ions were in excess.

The degree of supersaturation, S , existing at the end of the expansion has been calculated for a number of alcohols, esters, and acids; it is greatest for the acids and least for the alcohols. There is good agreement in some cases between the values of S deduced from the expansions and those calculated on the accepted theory of condensation on ionic nuclei.

In the case of certain acids, greater expansion is necessary to produce condensation in the absence of ionic nuclei than when they are present. The positive ions are more efficient condensing agents than the negative for certain organic vapours, but water condenses more easily on negative ions.

Certain organic compounds, including alcohols and esters, become negatively charged when air is bubbled through them, but acetic acid becomes positively charged. G. S.

Influence of Traces of Nitrous Gases on the Condensation of Water Vapour. ERICH PRINGAL (*Ann. Physik*, 1908, [iv], 26, 727—750).—The object of the experiments was to determine whether the condensing action of ordinary ozonised oxygen or air on water vapour is due to the presence of small quantities of nitrous gases. The experimental observations show that this is the case, and that pure ozone has no condensing action. In presence of water vapour, ozone appears to act on nitrogen and yield the condensation agent. Attention is called to the importance of these observations in connexion with the condensation of atmospheric water vapour. H. M. D.

Genesis of Ions by Collision of Positive and Negative Ions in a Gas. Experiments on Argon and Helium. E. W. B. GILL and F. B. PIDDECK (*Phil. Mag.*, 1908, [vi], 16, 280—290).—Townsend and Hurst (Abstr., 1905, ii, 7), assuming that positive and negative ions produce ionisation of a gas at definite rates, deduced an equation connecting gaseous conductivity and sparking potential with the gap between the electrodes. The authors have determined the minimum voltage required to produce a spark in argon or helium and the conductivity at various pressures in order to test the above theorem.

Each negative ion is supposed to produce α gaseous ions, and each positive ion β gaseous ions, in moving through a centimetre. Experiments were carried out with gaseous pressures of 0.66 mm. to 13 mm. and various distances between the electrodes. The values of the constants α and β at any one pressure could be calculated from three conductivity measurements. The remaining conductivities at this pressure were found to be in satisfactory agreement with Townsend and Hurst's equation. Additional support for the theory is found in the extremely close agreement between the sparking potentials determined directly in argon and helium and the potentials calculated from conductivity measurements at lower potentials. The values of the constants α and β for argon are greater than for air, so that argon is

more readily ionised than air by both positive and negative ions. The helium employed was somewhat impure, but as the theory holds equally well for mixtures, values of α and β could be calculated. Even impure helium is more readily ionised than hydrogen, and, after purification by charcoal cooled in liquid air, the sparking potential of helium was lowered (compare Strutt, *Trans. Roy. Soc.*, 1900, A, 193, 377). On the other hand, purification of the argon employed did not affect the values obtained with it.

After the passage of one spark, a higher potential was required to pass another immediately. Passing a spark in the reverse direction facilitated recovery. This effect may be due to some kind of polarisation at the zinc electrodes.

R. J. C.

Positive Electrons. A. BESTEMEYER (*Physikal. Zeitsch.*, 1908, 9, 541—542).—It has been found by J. Becquerel (this vol., ii, 751) that canal rays which are caused to pass through a small opening through which cathode rays are also passing are displaced in the immediate neighbourhood of the aperture under the influence of a magnetic field. Becquerel's conclusion, that the canal rays are temporarily transformed into positively-charged carriers as the result of contact with the cathode rays, is refuted by the author. The phenomenon can be satisfactorily explained by the electrostatic charge which the walls of the aperture receives as the result of bombardment by the cathode rays. In consequence of the action of this electrostatic charge, the canal rays are caused to deviate from their rectilinear paths.

H. M. D.

Experimental Investigation of the Stratified Positive Glow. R. HOLM (*Physikal. Zeitsch.*, 1908, 9, 558—562).—Measurements have been made of the potential gradient and the distance between adjacent strata of the positive glow in the discharge through hydrogen, nitrogen, and helium. Curves are plotted which show the dependence of these two factors on the current intensity. Almost identical results are obtained whether the method of Stark or that of H. A. Wilson is employed.

H. M. D.

Cathodic Volatilisation of Metals in Attenuated Gases. VOLKMAR KOHLSCHÜTTER (*Zeitsch. Elektrochem.*, 1908, 14, 417—421).—Fischer and Hähnel (this vol., ii, 653) have found that the volatilisation of a metal is the same in argon and hydrogen when the same current is used, whereas Kohlschütter and Goldschmidt (this vol., ii, 457) found large differences.

The author now shows that the results depend on the kind of current used. Two different induction coils are used: (A) a coil with a high resistance primary and low resistance secondary winding, and (B) an ordinary Ruhmkorff coil. Using platinum cathodes in tubes filled with hydrogen and argon respectively and connected in series, he finds that the quantity of platinum volatilised in argon is from four to twenty-two times as much as that volatilised in hydrogen.

The ratio of the quantities volatilised in argon and in hydrogen

is increased by increasing the pressure of the gas and the current strength when one coil is used, but decreased with the other coil. Hence the results obtained appear to depend entirely on the peculiarities of the induction coil employed. T. E.

Volatilisation of Cathodes in Attenuated Gases. FRANZ FISCHER and OTTO HÄHNEL (*Zeitsch. Elektrochem.*, 1908, 14, 433—437; VOLKMAR KOHLSCHÜTTER, *ibid.*, 437—439).—These papers contain the numerical data on which the statements already published (this vol., ii, 653) are founded, and a reply by Kohlschütter (compare preceding abstract). T. E.

Electrical Conductivity of Mixtures of Alcohol and Water. ANTONY G. DOROSCHESKY and M. S. ROSCHDESTVENSKY (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 887—908).—After discussing previous work on this subject, the authors give the results of their own measurements.

The values obtained for the conductivities of aqueous-alcoholic solutions of various concentrations at 15° are quite different from those given by Pfeiffer (Abstr., 1885, 1029; 1886, 4, 115), as also is the form of the curve connecting the conductivity with the percentage of alcohol by weight. The curve obtained by the authors not only exhibits no evidence of the existence of definite hydrates of alcohol, but has no singular points. In some respects it resembles the curves connecting the composition of aqueous alcoholic solutions with other properties, such as the specific gravity and boiling point, the curve falling sharply at both ends and remaining almost horizontal in the middle of its course; there is a slight rise corresponding with about 80% of alcohol.

When the concentration of the alcohol is expressed in grams per 100 c.c. of solution, the electrical conductivity follows the law $K_c \cdot c^{\frac{1}{2}} = \text{constant}$.

The electrical conductivities of aqueous solutions of alcohol are directly proportional to the dielectric constants of the solutions, and inversely proportional to their viscosities. T. H. P.

Electrical Conductivity of Liquid Sulphur. ALBERT WIGAND (*Ber. deut. physikal. Ges.*, 1908, 6, 495—508).—The author has made measurements of the electrical conductivity of liquid sulphur, in order to ascertain whether this is altered under the influence of light. The experiments were suggested by the fact that liquid sulphur, like solid selenium, consists of a mixture of two modifications in equilibrium, and that in the case of selenium, displacement of the equilibrium takes place under the influence of light in the direction of the formation of a larger proportion of the modification which has the greater conductivity. The results are negative, and indicate that the electrical conductivity of the soluble and insoluble forms of sulphur is the same.

Measurements of the conductivity at temperatures ranging from 130° to 446° show that this increases regularly up to 150°, where it reaches a maximum; it then falls, attaining a minimum value between

160° and 170°, above which it increases up to the boiling point. The view is expressed that the measured conductivity is really due to traces of foreign substances which are ionised in the molten sulphur.

H. M. D.

Effect of Concentration on the Temperature of Maximum Electrolytic Conductivity of Weak Electrolytes with Negative Heat of Dissociation. HENRIK WEGELIUS (*Zeitsch. Elektrochem.*, 1908, 14, 514—518).—Solutions of hypophosphorous acid (H_3PO_2) have a maximum conductivity at 72° for 5.75*N.*, 54° for 1.25*N.*, 52° for 0.995*N.*, 70° for 0.328*N.*, 87.5° for 0.12*N.* With weaker solutions, the temperature of maximum conductivity is higher than 100°. Phosphoric acid gave maxima at 77° for 2.715*N.*, 70° for 1.955*N.*, and at 79° for 0.217*N.*; weaker and stronger solutions showed no maximum at temperatures below 93°. An approximate theory showing how the temperature of maximum conductivity depends on the changes of dissociation and of ionic mobility with the temperature is given.

T. E.

A New Primary Voltaic Cell of the Daniell Type. JAMES STRACHAN (*Chem. News*, 1908, 98, 102).—The cell consists of an outer jar in which are placed a number of carbon rods connected by a leaden cover, through which passes a porous pot containing an amalgamated zinc rod immersed in a hydrochloric acid solution of zinc and ammonium chlorides. The outer jar contains an acid solution of lead tetrachloride prepared by dissolving freshly-precipitated lead peroxide in cold concentrated hydrochloric acid, or by adding concentrated hydrochloric acid to a mixture of lead acetate and bleaching powder contained in a pressure bottle and rapidly sealing the latter. Such a solution acts as a rapid depolariser, and is constant in its action; the cell has a higher *E.M.F.*, but a much lower resistance, than a Daniell cell. The disadvantage of the cell due to the escape of chlorine may be overcome by sealing the space between the leaden cover and the porous pot with paraffin wax. The zinc may be replaced by iron, but the *E.M.F.* drops then from 1.5 to 0.95.

P. H.

Gas Electrodes. I. Nitric Oxide. Ugo Grassi (*Nuovo Cim.*, 1908, [v], 15, 467—480).—The potential of a platinised platinum electrode, saturated with nitric oxide, was measured against a normal calomel electrode. In acid solutions, the electrode is stable, and its potential is independent of the rate of passage of the gas; in alkaline solutions the difference of potential changes sign in the first minute, and only attains its final value slowly. This is due to the conversion of the oxide into alkali nitrite and nitrous oxide, which is greatly accelerated by platinum. The first stage of the reaction is the formation of sodium nitrohydroxylamate: $2\text{NO} + \text{Na}_2\text{O} = \text{ON}:\text{N}(\text{ONa})_2$, which then decomposes according to the equation $2\text{Na}_2\text{N}_2\text{O}_3 + \text{H}_2\text{O} = 2\text{NaNO}_2 + 2\text{NaOH} + \text{N}_2\text{O}$. Quantitative experiments show that the nitric oxide reacts in solution as a double molecule. In acid solutions, the cell $\text{H}-(\text{NO})_2-\text{NO}$ has an *E.M.F.* of 0.80 volt, nitric oxide being positive to hydrogen.

C. H. D.

Potential of a Hydrogen Electrode in Acid and Alkaline Solutions. C. L. A. SCHMIDT and C. P. FINGER (*J. Physical Chem.*, 1908, 12, 406—416).—The authors have measured the potential of a hydrogen electrode in a series of solutions, each containing 0.25 gram-atom of boron per litre and prepared by mixing solutions of boric acid and borax or sodium hydroxide in different proportions. From the values of the potential difference, the hydrogen-ion concentrations are calculated, and a series of readily reproducible standards for the colorimetric determination of the strengths of acids and bases has been provided.

From the form of the curve, which is obtained by plotting the potential differences against the percentage amount of the hydrogen of the boric acid which is replaced by sodium, the conclusion is drawn that the compound NaH_2BO_3 (or its anhydride, NaBO_2) is the only one formed to any appreciable extent when solutions of boric acid and sodium hydroxide are mixed. This conclusion is in agreement with the results of thermochemical and freezing-point measurements.

H. M. D.

Solid Electrolytes. Their Decomposition by a Current and their Electromotive Properties in Galvanic Chains. FRITZ HABER (*Ann. Physik*, 1908, [iv], 23, 927—973).—Part of this paper represents a summary of work which has been published in detail previously (compare Haber and Tolloczko, *Abstr.*, 1904, ii, 813; Haber and Moser, *Abstr.*, 1905, ii, 667; Haber and Foster, *Abstr.*, 1907, ii, 66; Haber and Fleischmann, *Abstr.*, 1907, ii, 6; Haber, Rieff, and Vogt, this vol., ii, 254).

In the third section [with G. BIRNSTEIN], experiments on the electrolytic decomposition of solid salts of the alkali metals are described. Pure potassium chloride yields at the cathode a violet substance which dissolves in water with evolution of hydrogen. It is not acted on by anhydrous ethyl alcohol. The eutectic mixture of potassium and sodium chloride yields a yellowish-brown substance with the same properties. On electrolysing a mixture of sodium chloride and carbonate, carbon separates at the cathode. Potential measurements are recorded which support the view that the coloured substances formed at the cathode are sub-chlorides of the alkali metals.

The last section of the paper [with R. BETTNER] deals with the potential differences at the surfaces of contact of solid electrolytes and of solid salts and their saturated solutions. Application is made of Nernst's theory of potential differences to the special systems under investigation, and a number of theoretical deductions are made.

H. M. D.

Explanation of Supertension. ERICH MÜLLER (*Zeitsch. Electrochem.*, 1908, 14, 429—433). Compare Kaudler, *Abstr.*, 1907, ii, 924, and this vol., ii, 558).—Polemical.

T. E.

Electrolytic Properties of Dilute Solutions of Sulphuric Acid. W. C. DAMPIER WHEATHAM and H. H. PAINE (*Proc. Roy. Soc.*, 1908, 81, 4, 58—80). Compare *Abstr.*, 1906, ii, 69).—It has been

shown in a previous paper that the progressive diminution in the equivalent conductivity of dilute sulphuric acid with dilution when the concentration is less than 0.0005—0.001 gram-equivalent per litre is still observed when the solvent is boiled repeatedly under low pressure and the air re-admitted through potash bulbs (to remove carbon dioxide), and it is now shown that the diminution in question persists when the air is re-admitted through bulbs containing dilute sulphuric acid and potassium hydroxide respectively.

The observed diminution in the equivalent conductivity could be accounted for if the H^+ ion travels more slowly in dilute than in concentrated solutions, and to test this point the transport ratio of solutions of different concentration has been determined by a modification of the ordinary method, the changes in concentration round the electrodes due to electrolysis being determined by measuring the conductivity of the solution; in the case of the very dilute solutions, with pairs of electrodes placed in the anode and cathode compartments respectively. Although a change in the expected direction was actually observed, the transport ratio apparently increasing from 0.186 to 0.202 on progressive dilution, it is not considered probable that this is due to a change in the relative migration velocity of the ions, but to some alkaline or saline impurity in the water. As the effect in question is not removed by boiling, the impurity might be ammonium carbonate, but the matter is not regarded as being finally settled.

G. S.

Electrolysis of Copper Solutions. JEAN MEYER (*Bull. Soc. chim. Belg.*, 1908, 22, 259—291).—The author attempts to find a more satisfactory explanation of the anomalous behaviour of the copper voltameter than that provided by the theories of Foerster, Abel, and others. The Foerster-Seidel theory requires that a gram-molecule of cuprous oxide for each 2×96540 coulombs should be formed on electrolysis of a hot solution of copper sulphate at a lower potential than that required for the deposition of copper; on repeating these authors' experiments, however, it was found that the weight of the oxide was less than half this. Similar results were obtained when operating in absence of air, hence the deficit cannot be due to oxidation to copper sulphate. When the electrolysis is carried out at 90° , a green basic salt of variable composition is precipitated; this compound, which appears to be identical with that obtained by boiling an aqueous solution of copper sulphate, probably arises from dissolution of the cuprous oxide in the copper sulphate solution. This secondary dissolution of the oxide, which is independent of the current and the concentration of the ions, explains the presence of a cuprous salt, and evidence is adduced to show that it accounts for the formation of cuprous oxide at both electrodes. At the cathode, the following reaction is supposed to occur: $Cu + CuSO_4 + H_2O \rightleftharpoons Cu_2O + H_2SO_4$. The same principle is applied to cover the phenomena observed when solutions of cupric chloride are electrolysed.

It was found possible to estimate the amount of cuprous oxide in the metallic deposits by treating the mixture with a neutral

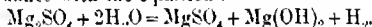
solution of ferric alum, which, after being acidified with sulphuric acid, was titrated by permanganate.

It is pointed out that Bose's phenomenon cannot be due to the partial discharge of cupric ions: $\text{Cu}^{++} \rightarrow \text{Cu}^+$, as Abel has suggested, since, by electrolysing a hot acid solution of copper sulphate in absence of oxygen and operating with currents of low density, a good yield of pure copper is obtained, the dissolution of copper in copper sulphate solution being accomplished as readily in acid as in neutral solution (compare Heiberg, *Abstr.*, 1903, ii, 263).

In the hope of obtaining a perfect voltametric solution, hydrogen peroxide, instead of sulphuric acid, was added to the copper sulphate in order to prevent the formation of cuprous salts. The results, however, were not satisfactory, probably owing to the formation of persulphates and catalytic decomposition of the hydrogen peroxide at the electrodes.

W. O. W.

Reversed Electrolysis. J. W. TURRENTINE (*J. Physical Chem.*, 1908, 12, 448—467).—A number of apparently anomalous electrolytic phenomena, which are in reality due to secondary reactions, have been examined. When a current is passed through a solution of sodium sulphate between a magnesium anode and a platinum cathode, hydrogen is evolved at the anode, which becomes covered with scales of magnesium hydroxide. It is supposed that the magnesium dissolves at the anode as a univalent metal, a secondary reaction then taking place in accordance with the equation:



In a similar way, hydrogen is evolved at an aluminium anode in the electrolysis of a solution of sodium chloride. It is not possible to determine the effective valence with which solution takes place.

When a solution of potassium permanganate acidified with sulphuric acid is electrolysed between platinum electrodes, the gas evolved at the cathode contains a considerable proportion of oxygen. This has been traced to the decomposition of hydrogen peroxide formed by the electrolytic reduction of manganese dioxide.

H. M. D.

Migration of Ions in Heterogeneous Systems. KARL SPIRO and LAWRENCE J. HENDERSON (*Zeitsch. Chem. Ind. Kolloide*, 1908, 3, 91—92).—Solutions of phosphates, carbonates, and globulins of the same composition are separated by a membrane, on one side of which a substance such as calcium carbonate, magnesia, or globulin is suspended. When carbon dioxide is passed through the solution which does not contain the suspended matter, its alkalinity to methyl-orange increases; the increase is diminished by passing in oxygen. This arrangement behaves in the same way as blood, and the experiments show that the phenomena are due to simple diffusion, and the assumption of a selective permeability of the walls of the red corpuscles under the influence of carbon dioxide is unnecessary.

T. E.

The Part Played by Ionisation in Certain Chemical Reactions. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1908, 305—306).—The double decomposition between soluble chlorides

and insoluble carbonates in the presence of water is due to the ionisation of the soluble salt; thus in the case of potassium chloride and barium carbonate a small part of the dissociated salt reacts with the barium carbonate to form barium chloride and potassium carbonate.

M. A. W.

Estimation of the Hydration of Ions from Measurements of Electromotive Forces. GILBERT N. LEWIS (*Zeitsch. Elektrochem.*, 1908, 14, 509—510; *J. Amer. Chem. Soc.*, 1908, 30, 1355—1357).—The *E.M.F.* of a concentration cell depends on the ratio of the "activities" of both the electrolyte and the water in the two solutions (this vol., ii, 16), and on the numbers of ions and molecules of water transported by the current. A measurement of the *E.M.F.* of a cell in which the electrolyte has the same concentration in each solution and therefore the same activity, whilst the activity of the water in one solution is altered by the addition of a non-electrolyte, should make it possible to estimate the number of molecules of water carried along with the ions of the electrolyte.

T. E.

Improved Apparatus for the Measurement of Transference Numbers in Solutions of the Halogen Acids and their Salts. EDWARD W. WASHBURN (*Technology Quart.*, 1908, 21, 164—177).—The essentially new features of the author's apparatus are represented by the special form of the silver anode and the silver halide cathode. The anode consists of a silver wire wound into a flat spiral, which is placed at the bottom of a Soxhlet extraction cartridge, this being filled with small crystals of electrolytic silver, which are packed tightly round the silver wire. This arrangement gives an electrode of very large active surface. Using a cartridge 6 cms. long and 1.9 cms. in diameter, an electrode prepared in this way will carry a current of 0.1 ampere for sixteen hours without the formation of the slightest trace of acid or of colloidal silver chloride.

The cathode consists of a silver disk prepared by making it the anode in the electrolysis of a solution of sodium chloride. The disk, which just fits into the apparatus, is covered with a layer of silver chloride, obtained by precipitating a hot solution of silver nitrate with excess of an alkali chloride solution. An electrode, 2.3 cms. in diameter, is able to carry a current of 0.5 ampere without the evolution of hydrogen or the formation of the slightest trace of alkali.

The anode and cathode tubes of the apparatus are provided with stopcocks, and are connected by means of a ground-glass joint.

H. M. D.

Hydrolysis of Salts in Solution: Lecture Experiment BARTOLO L. VANZETTI (*Gazzetta*, 1908, 38, ii, 98—99).—The following simple experiment renders evident the phenomenon of hydrolysis of salts. A test-tube is filled to about three-fourths of its height with a 5–10% gelatin solution containing faintly alkaline phenolphthalein. When the gelatin has solidified, a 10% ferric chloride solution is

poured on to it. As diffusion into the gelatin proceeds, two strata become more and more distinct, the lower one being colourless, owing to the more rapid diffusion of the acid liberated by hydrolysis, and the less advanced, opaque one consisting of ferric hydroxide. Salt, such as nickel chloride or copper sulphate, containing a coloured ion may also be used.

T. H. P.

Change of Colour of Phenolphthalein. RUDOLF WEGSCHEIDER [with A. SCHUGOWITSCH] (*Zeitsch. Elektrochem.*, 1908, 14, 510-512. Compare Abstr., 1904, ii, 512; this vol., ii, 646).—The concentration of the red ions in dilute alcoholic solutions containing known quantities of phenolphthalein and sodium hydroxide is determined by comparison of the colour with solutions containing an excess of sodium hydroxide. It is found that the expression $[RH][OH]/R'$ (where R' represents the phenolphthalein ion) is only approximately constant when there are more than two molecules of sodium hydroxide for each molecule of phenolphthalein in solution. On the assumption that the red salt contains two atoms of sodium (Abstr., 1905, i, 440), and that it is hydrolysed thus: $R' + H_2O \rightleftharpoons RH' + OH'$ and $RH' + H_2O \rightleftharpoons RH_2 + OH'$, a satisfactory explanation of the results obtained is possible.

T. E.

New Method for Determining the Specific Heats of Liquids. THEODORE W. RICHARDS and ALLAN WINTER ROWE (*Zeitsch. physikal. Chem.*, 1908, 64, 187-200).—The liquids, the specific heats of which are to be compared (for example, water and a salt solution), are successively put in the calorimeter, and a definite quantity of heat is developed each time by neutralising a given quantity of acid with alkali in a platinum vessel, which is immersed in the liquid of the calorimeter. The calorimeter itself is completely surrounded by a jacket, the temperature of which is constantly adjusted to the changing temperature of the calorimeter (see Richards, Henderson, and Forbes, Abstr., 1905, ii, 677; Richards, Henderson, and Frevert, Abstr., 1907, ii, 604). The rise of temperature, therefore, in the calorimeter takes place adiabatically. The same apparatus may obviously be employed in the determination of heats of dilution.

One or two experiments made with this apparatus are recorded. The specific heat of a hydrochloric acid solution of the composition $HCl + 200H_2O$ has been found to be 0.9809, and the maximum deviation from this figure in four independent experiments was 0.02%. The heat developed when a solution of the composition $NaOH + 5.25H_2O$ is diluted until it has the composition $NaOH + 43.5H_2O$ is 5.79 kilojoules.

J. C. P.

Specific Heats and Heats of Fusion of Isomorphous Substances and their Mixtures. A. BOGOJAWLENSKY and N. WINOGRADOFF (*Zeitsch. physikal. Chem.*, 1904, 64, 251-254).—The authors have determined the specific heats and latent heats of fusion for mixtures of (1) *m*-chloronitrobenzene and *m*-bromonitrobenzene, (2) α -chlorocinnamaldehyde and α -bromocinnamaldehyde, (3) azobenzene and dibenzyl. They find that the specific heats of these

isomorphous mixtures, in both the liquid and the solid state, can be calculated by the mixture rule. In the first two cases, the latent heat of fusion (f) can be calculated by the mixture formula $f = (f_1 p_1 + f_2 p_2) / (p_1 + p_2)$ in fair agreement with the observed values, but in the third case there are marked discrepancies, the observed values being regularly less than the calculated values. It is noted that only in this third case does the freezing-point curve exhibit a minimum, and that the discrepancies referred to are similar to those observed with substances which form a eutectic mixture.

J. C. P.

Specific Heat of Mercury. W. A. KURBATOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 811—813).—The results of a number of measurements show that the mean specific heat of mercury from 0° to 306° is 0.0325—0.0331. This value, together with that previously obtained by the author (*Abstr.*, 1903, ii, 139), and those of other investigators, prove that the specific heat of mercury rises distinctly as the boiling point is approached.

In general, the specific heat of substances, the molecules of which do not change from the melting point to the critical temperature, is represented by a curve approximating to a straight line, and the true specific heat is the minimum between these two temperatures.

T. H. P.

Specific Heat of Alcohol and of its Mixtures with Water. ANTONY G. DOROSCHESKY and ADAM W. RAKOWSKY (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 860—886).—The authors discuss the various formulae which have been proposed for expressing the specific heat of alcohol at different temperatures, and come to the conclusion that all these formulae refer, not to absolute alcohol, but to alcohols containing small, and probably varying, proportions of water. For carefully dehydrated alcohol, the value 0.6597 is obtained as the mean specific heat at 22—99°; this gives the value 0.518 for the specific heat at 20°, taking the value 0.0035 given by Hirn's measurements (*Ann. Chim. Phys.*, 1867, [iv], 10, 32) for the temperature-coefficient between 20° and 10°. For the alcohol used by the authors, D_{15}^{20} 0.79426 and k at 15° is 0.07×10^{-6} ohms.

In general, the changes of specific heat (C) of mixtures of alcohol and water with temperature are irregular. Thus, for 10—10% aqueous alcohol solutions, $C_{0-15} > C_{0-20} > C_{0-4} < C_{0-4} < C_{0-15}$, and for 10—20% solutions, $C_{0-15} > C_{0-20}$.

For solutions containing 100—50% of alcohol, the specific heat is expressed by the equation: $C = 0.6628 + 0.007345 (100 - p) - 0.000145 (100 - p)^2$, where p represents the % of alcohol by weight in the solution. For 50—20% solutions, $C = 0.9475 + 0.005164 (50 - p) - 0.0000625 (50 - p)^2$, and for 20—0% solutions, $C = 1.0455 - 0.00104 (20.09 - p) - 0.0000482 (20.09 - p)^2$.

The authors' results show that Thomsen's supposition (*Thermoch. Untersuch.*, 1882, vol. i, 74), that at their boiling points the heat effect of the formation of aqueous alcoholic solutions is zero, is not general, but applies only to one definite solution. The temperature

at which the mixing has a zero heat effect is below the boiling point for strong solutions, and above the boiling point for dilute solutions of alcohol.

T. H. P.

Equation of Condition for Metals: Correction. MAX THIESEN (*Ber. deut. phys. Ges.*, 1908, 8, 604).—According to Grüneisen (this vol., ii, 563), for those metals which have been sufficiently investigated, the relation between the specific heat and the coefficient of expansion is nearly independent of the temperature. In deriving the form of the temperature function of these two magnitudes (this vol., ii, 659), the author assumed that the θ of equation 4 (*loc. cit.*) was a pure temperature function, an assumption which is not justified. The value of θ is given only by a partial differential equation, which leaves the form of the temperature function undetermined. The relations given by the author do not, therefore, follow as consequences of Grüneisen's experimental law, but must be tested by direct experiment, as has been done in the case of platinum.

T. H. P.

Melting-point and Freezing-point Curves of Binary Systems when the Solid Phase is a Mixture (Amorphous Solid Solution or Mixed Crystals) of the Two Components. JOHANNES J. VAN LAAR (*Zeitsch. physikal. Chem.*, 1908, 64, 257—297).—A mathematical discussion of the possible forms of curve. In the case of optical isomerides and tautomeric substances, a minimum or eutectic point in the freezing-point curve is impossible (compare Roozeboom, *Abstr.*, 1899, ii, 355, 401). When a racemic compound is formed, two eutectic points are possible. The formation of liquid mixed crystals is also discussed.

In Tammann's method of representing the total heat-content of binary systems (this vol., ii, 660), the heat of mixing may only be neglected in comparison with the heat of fusion so long as only stable systems are dealt with. In the labile region below the eutectic point, the heat of mixing may be considerable.

C. H. D.

Reciprocal Salt-pairs. I. ERNST JANECKE (*Zeitsch. physikal. Chem.*, 1908, 64, 305—327. Compare Meyerhoffer, *Abstr.*, 1901, ii, 639).—The conditions occurring in the melting and solidifying of reciprocal pairs of salts, in which there is an equilibrium $M'R + M''R' \rightleftharpoons M'R' + M''R$, when only one liquid phase is present, are discussed for the two cases: (a) when the only solid phases are the four salts; (b) when only two isomorphous mixtures separate. The equilibrium diagrams for case (a) are completely discussed. In case (b) there are many possibilities. The simplest conditions occur when the melting points of each pair of reciprocal salts have neither a maximum nor a minimum point; the whole system may then be broken up into two ternary systems.

The eutectic curve between the two solid phases may be without any maximum or minimum, or may have either a maximum or a minimum. The last of these cases is illustrated by the system $(K_2, Na_2) - (Cl_2, SO_4)$ (this vol., ii, 841).

C. H. D.

Character of Melting-Point and Clearing-Point Curves for Fluid-Crystalline Substances and their Mixtures. II. ALEX. BOGOJAWLENSKY and N. WINOGRADOFF (*Zeitsch. physikal. Chem.*, 1908, 64, 229—242. Compare Abstr., 1907, ii, 844).—The method described in the earlier paper has been applied to other binary mixtures, namely, (1) *p*-azophenetole + *p*-azoanisolephenetole, (2) *p*-ethylpropylazophenol + *p*-methylpropylazophenol, (3) *p*-azoanisole + *p*-azoanisolephenetole, (4) *p*-azophenetole + *p*-dipropylazophenol, (5) *p*-azoanisolephenetole + *p*-dipropylazophenol, (6) *p*-azoanisolephenetole + azoxyanisole, (7) *p*-azoxyphenetole + *p*-azoanisolephenetole, (8) *p*-methylpropylazophenol + *p*-azoanisole, (9) *p*-methylpropylazophenol + dipropylazophenol.

The melting-point curves obtained in cases (1) and (2) show that complete series of mixed crystals are formed; the melting-point curves obtained in cases (3) and (4) exhibit a minimum, but it is not certain whether this is an eutectic or not; in cases (5), (6), and (7) the melting-point curves are all marked by eutectics; in cases (8) and (9) the melting-point curves were not traced.

The clearing-point curves show that in all cases the fluid-crystalline phases are completely miscible. The direction of these curves depends exclusively on the clearing points of the two components, and is independent of the course of the melting-point curve. Hence it comes that, as in cases (1) and (2), two substances the clearing points of which lie below their respective melting points form fluid-crystalline mixtures within certain limits of concentration. In cases where the labile clearing point of one component cannot be determined directly, owing to the impossibility of supercooling, it may be ascertained by extrapolating the clearing-point curve, which in the majority of cases is nearly a straight line.

The melting points and clearing points for various azo- and azoxy-compounds are as follows, the melting point being given first in each case: azoanisole 164.1°, 108.0°; azophenetole, 160.2°, 156.1°; *n*-dipropylazophenol, 146.1°, 112.0°; ethyl-*n*-propylazophenol, 144.2°, 139.6°; methylethylazophenol, 131.5°, 132.2°; methyl-*n*-propylazophenol, 113.1°, 110.0°; azoxyphenetole, 136.9°, 167.5°; azoxyanisole, 117.4°, 134.4°; *n*-dipropylazoxyphenol, 116.0°, 122.0°; azoxyanisolephenetole, 93.5°, 149.6°. It will be observed that all the azo-compounds are monotropic, that is, their clearing points lie below their melting points, whilst the azoxy-compounds are enantiotropic.

J. C. P.

Inverse Melting Points. J. N. BRÖNSTED (*Zeitsch. physikal. Chem.*, 1908, 64, 374—377).—The course of the solubility curves for the hydrates of ceric sulphate (Koppel, Abstr., 1904, ii, 819) indicates that two of the hydrates, $\text{Ce}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Ce}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$, are only stable at higher temperatures, passing into the octahydrate and the tetrahydrate at 35° and 100° respectively. Since this would mean the conversion of a solid hydrate into a lower hydrate and an aqueous solution on cooling, the temperatures mentioned may be regarded as inverse melting points. Such fusion on cooling was not directly observed, but is a thermodynamical consequence of the position of the solubility curves.

It is shown on theoretical grounds that inverse melting points can

only occur when, as is the case with ceric sulphate, the solubility of the salt diminishes with increasing temperature. C. H. D.

A Modification of the Cryoscopic Method for Investigating Small Quantities of liquid. TOSAKU KINOSHITA (*Biochem. Zeitsch.*, 1908, 12, 390—406).—With certain modifications, the Beckmann method can be applied to small quantities of liquid. The chief of these consists in enveloping the thermometer bulb with a thin layer of paraffin, ash-free filter-paper, and sheet-rubber. S. B. S.

Analysis of the Lowering of the Freezing Point in Physiological Fluids. II. Lowering of the Freezing Point of Suspensions. ERNST TEZNER and JOHANN ROSKA (*Zeitsch. physiol. Chem.*, 1908, 56, 495—506).—The depression of the freezing point of water by the addition of a fatty acid is not nearly so marked when solid particles, such as blood-charcoal or casein, are suspended in the solution. This effect is attributed to adsorption, which produces a concentration of the solute around the solid particles, and thus diminishes the concentration of the rest of the solution.

The adsorption depends mainly on the surface tension, and this again on the concentrations of the various dissolved materials, but is not directly proportional to their osmotic concentrations. Hence the lowering of the freezing point of such solutions is not a simple function of the osmotic concentration.

Negative adsorption is not met with. The process of filtration yields a liquid with the same or greater lowering of the freezing point, according as the filtration is more or less complete. J. J. S.

Influence of the Rate of Cooling on the Composition of Saturated Mixed Crystals. W. VON LEFKOWSKI (*Zeitsch. anorg. Chem.*, 1908, 59, 285—292).—Experiments have been made to ascertain whether molten alloys of bismuth and tin and of copper and silver give rise to mixed crystals when rapidly cooled. The supersaturation phenomena requisite for the production of these crystals are found in the case of bismuth-tin alloys, but not in the case of copper-silver alloys.

Alloys containing up to a little more than 1% of tin show no trace of the eutectic mixture when rapidly cooled, but this is found if the percentage of tin exceeds 1.5. The supersaturated mixed crystals, which are formed in the first case, are unaltered by exposure for six hours at 120°.

The difference in behaviour of bismuth compared with copper and silver is attributed to the greater velocity of crystallisation of the supercooled metal in the case of bismuth. H. M. D.

Vaporisation. II. HANSS VON JÜPTNER (*Zeitsch. physikal. Chem.*, 1908, 63, 579—618. Compare this vol., ii, 663).—Starting with van der Waals' equation, the author deduces formulae for the calculation (1) of the internal pressure, $\pi = a/v^2$, due to molecular attraction; (2) of the fraction of the total volume actually occupied by the molecules. The values of these are then deduced for a large number

of substances. It is found that the value of a , in general, increases with the molecular weight, although constitutive influences make themselves felt. From these values of a , the critical constants are calculated, and the expressions $(p_k + \pi_k)/p_k = A$ and $v_k/v_k = B$ [v_k = ideal volume] are evaluated. It is shown that, in general, A increases with B . The question how far these various quantities are affected by molecular association at the critical temperature is also discussed. The term b in van der Waals' equation is regarded as variable with the temperature and internal pressure, possibly also with the attraction of neighbouring molecules.

J. C. P.

Determination of Vapour Pressures of Solutions with the Morley Gauge. OLIN F. TOWER (*J. Amer. Chem. Soc.*, 1908, 30, 1219—1228).—The methods most commonly used for determining the vapour pressures of solutions are of two kinds, which may be distinguished as the "differential" and the "dynamic" methods. In the former, the difference between the two vapour pressures, such as that of a given solvent and one of its solutions, is measured by means of a suitable gauge, whilst the latter method is based on the principle that when air, or some other inactive gas, is saturated with the vapour of the liquid or solution, the following relation holds: total volume/volume of the aqueous vapour = total pressure/pressure of the aqueous vapour. Ostwald has simplified this method by allowing the air to bubble first through the solution and then through pure water.

A method has now been studied which is of the "differential" class, and resembles that of Smits, except that his micromanometer is replaced by a mercury gauge, designed by Morley (*Amer. J. Sci.*, 1902, 13, 455) for measuring small differences of pressure. Determinations have been made of the vapour pressures of aqueous solutions of sucrose, potassium iodide, and lithium chloride, and of methyl- and ethyl-alcoholic solutions of tetraethylammonium iodide, potassium iodide, and lithium chloride. The results are tabulated.

It has been found that this method involves several difficulties and sources of error. The readings vary considerably, and it is therefore necessary to make a great many readings and take the average. The time occupied in this way, and also in repairing breaks and overcoming other difficulties, is very great. Moreover, the solutions must always be maintained at a temperature lower than that of the gauge. For these reasons, this "differential" method is regarded as less trustworthy, and subject to more limitations than the "dynamic" or air-bubble method.

E. G.

Osmotic Researches. I. ERNST COHEN and J. W. COMMELIN (*Zeitsch. physikal. Chem.*, 1908, 64, 1—52).—The authors review the attempts which have been made to measure osmotic pressure directly, and criticize in detail Kahlenberg's experimental methods and conclusions (*Abstr.*, 1906, ii, 337). An osmotic apparatus has been devised in which the weaknesses of Kahlenberg's osmometer are remedied, and with which the osmotic pressure of sucrose in pyridine has been determined. As in Kahlenberg's experiments, the semipermeable membrane was of india-rubber. The authors show that it

is immaterial whether the contents of the osmotic cell are stirred or not. It has not been found possible to get consistent values for the osmotic pressure in parallel experiments, and all the pressures recorded were far below the theoretical values. The authors consider it probable that water is responsible for the irregular results obtained, for it has been found that the presence of water either in the solution or in the pure solvent exerts a very marked influence on the observed pressure. Fresh experiments are therefore planned in which perfectly anhydrous pyridine will be employed.

J. C. P.

[Vapour Pressure of Dry and of Ordinary Sal Ammoniac.]
RICHARD AREGG (*Zeitsch. physikal. Chem.*, 1908, 63, 623—624).—A reply to van Laar (this vol., ii, 569).

J. C. P.

The Avogadro-Guldberg Law. W. A. KURBATOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 813—817).—It was shown by Guldberg that the absolute boiling points of different substances represent "corresponding" temperatures, as they are always two-thirds of the absolute critical temperatures. The author finds, however, that this relation is considerably influenced by various factors, and, on the basis of a large number of experimental numbers given by various investigators, he formulates the relationship between boiling point and critical temperature as follows. With all substances having less than five atoms in the molecule, and having, also, low molecular weights, the ratio of boiling point to critical temperature has the mean value 0.666. The ratio varies, however, from 0.580 for the lower members of a homologous series to 0.700 for the highest members investigated.

T. H. P.

Calculation of Thermochemical Constants. V. Calculation of the Thermal Constants of Aromatic Substances. H. STANLEY REIDGROVE (*Chem. News*, 1908, 98, 80). Compare this vol., ii, 564).—The author gives in tabular form a comparison of the molecular heats of combustion and formation as determined by Thomsen, and as calculated by himself for toluene, mesitylene, ψ -cumene, chlorobenzene, anisole, and phenol. The method of calculation does not necessitate any assumption concerning the constitution of benzene. The figures show that the various groups exhibit the same thermal behaviour in aromatic as in aliphatic compounds.

P. H.

Free Energy Changes Attending the Formation of Certain Carbonates and Hydroxides. JOHN JOHNSTON (*J. Amer. Chem. Soc.*, 1908, 30, 1357—1365). Compare this vol., ii, 358).—The increase of free energy attending the conversion of a hydroxide into the oxide and water vapour, and of a carbonate into the oxide and carbon dioxide, can be expressed by the equation $\Delta F = \Delta H + kT \log p + IT$ (ΔH being the increase in total energy). Calculations from existing pressure data for the hydroxides and carbonates of magnesium, calcium, lithium, strontium, and barium give, in general, very concordant values for I , the thermodynamically undetermined constant.

The increase in free energy at 25°, accompanying the formation of these substances, and their dissociation pressures at 25° have been calculated. The results show that the stability of the hydroxides and carbonates increases in the order magnesium, calcium, lithium, strontium, barium, sodium.

It is shown that neither Le Chatelier and de Forcrand's rule, $T = \Delta H/30$, nor Nernst's approximate formula for heterogeneous equilibria, $\log p = \Delta H/4.576T + 1.75 \log T + C$, can lead to accurate results, except in special cases.

E. G.

Hydrolysis as Illustrated by Heats of Neutralisation.

VICTOR H. VELEY (*Trans. Faraday Soc.*, 1908, 4, 19—26. Compare Lundén, this vol., ii, 164).—The paper contains a summary of the available data as to the acid and basic dissociation constants of a number of weak bases and acids and the degree of hydrolysis of their salts, as determined by Bredig, Winkelblech, Walker, Lundén, and the author. The heats of neutralisation determined directly of these weak bases and acids are also given as far as available, as are the values calculated by Lundén and others by means of the van t'Hoff equation connecting heat development and displacement of equilibrium. The data appear to show that the higher the value for the heat of neutralisation the less is the degree of hydrolysis, and conversely.

G. S.

Orthobaric Volumes in Relation to Pressure and Temperature.

EDWARD HAIGH (*Phil. Mag.*, 1908, [vi], 16, 201—223); SYDNEY YOUNG (*ibid.*, 222—223).—Haigh puts forward a dual equation to express the relation of the orthobaric volumes of liquid and saturated vapour to vapour pressure and temperature of ebullition. At the critical point, the dual equation reduces to the well-known van der Waals' form. The dual equation affords results which are in excellent accord with the experimental values in the cases of fluorobenzene, isopentane, benzene, and a number of other hydrocarbons. The small deviations observed with methyl and propyl alcohols, carbon tetrachloride, and stannic chloride are explainable as polymerisation effects and experimental errors.

With a liquid far removed from its critical point, a small experimental error in the volume is greatly magnified, and the spheres of action of the molecules may intersect. The theorem may be utilised to test the accepted values of the critical constants of a substance, for on combining them with the data of observations at temperatures below the critical point, the dual equation should hold good.

From the specific volumes of isopentane liquid and vapour at temperatures between 10° and 120°, the critical volume of this substance is calculated to be 4.2686, whereas Young obtained the value 4.266 experimentally.

This agreement does not constitute an independent proof of the validity of the dual equation, since the value of the critical volume (4.266) was assumed for the purposes of the former proof. R. J. C.

Saturated Aqueous Solutions of Sparingly Soluble Salts. II. The Amounts Dissolved and their Alteration with Temperature. FRIEDRICH KOHLRAUSCH (*Zeitsch. physikal. Chem.*, 1908, 64, 129—169. Compare Abstr., 1903, ii, 528).—The experimental material previously collected (*loc. cit.*) has been subjected to recalculation, with the result that some of the values for the solubility already communicated (Abstr., 1905, ii, 152) have undergone alteration. In this extension of the work, special attention has been paid to ascertaining the value of the equivalent conductivity which should be employed in calculating the solubility from the specific conductivity of the saturated solution. It is only in the case of salts with extremely low solubility that λ_{∞} can safely be taken as the equivalent conductivity of the saturated solution. The correct value can, however, be ascertained on the basis of the rule that in dilute solutions λ changes almost proportionally with the square root of the concentration. For details of the way in which this rule is applied to the different salts, the original must be consulted. Another point to which attention has been paid in this extension of the work, is the evaluation of the solubility for temperatures other than 18°.

The following is a list of the salts for the solubility of which an appreciably different value has been found on recalculation; the number given after each salt represents the weight in milligrams present in a litre of the saturated solution at 18°: magnesium fluoride, 87; silver chloride, 1.34; silver iodate, 38.5; lead iodate, 17.8; barium chromate, 3.5; lead chromate, 0.1; barium oxalate ($\text{BaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$), 85.1; barium oxalate ($\text{BaC}_2\text{O}_4 \cdot 3\frac{1}{2}\text{H}_2\text{O}$), 105. In addition, numbers are given for the following minerals: fluorite, 15.0; barytes, 2.6; celestine, 114.3.

For the values of the solubility at temperatures other than 18°, the original must be consulted. Of the salts examined, magnesium fluoride is the only one the solubility of which diminishes as the temperature rises. J. C. P.

Studies of the Processes Operative in Solutions. VI. Hydrolysis, Hydrolation, and Hydronation as Determinants of the Properties of Aqueous Solutions. HENRY E. ARMSTRONG (*Proc. Roy. Soc.*, 1908, 81, 1, 80—95. Compare Abstr., 1907, ii, 848, 849, 856).—Water is regarded as a complex mixture of active and inactive molecules, the active components are monad *hytrone* (H_2O) molecules and *hydrol-hytrone* (briefly hydronol or hydrol) molecules,

$\text{H}_2\text{O} \begin{smallmatrix} \text{H} \\ \diagup \text{O} \diagdown \\ \text{OH} \end{smallmatrix}$; the inactive molecules are a series of polyhydrones (formed by association unaccompanied by rearrangement) of the form $\text{H}_2\text{O}:\text{OH}_2$, $\text{H}_2\text{O} \begin{smallmatrix} \text{OH}_2 \\ \diagup \text{O} \diagdown \\ \text{OH}_2 \end{smallmatrix}$, &c.

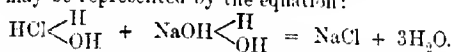
When non-electrolytes of the type RX are dissolved in water, interaction takes place with the hydrol molecules present in the solvent, with the ultimate possible production of active complexes, $\text{RX} \begin{smallmatrix} \text{H} \\ \diagup \text{O} \diagdown \\ \text{OH} \end{smallmatrix}$, inactive hydrone complexes, $\text{RX}:\text{OH}_2$, and polymerides of the type $\text{RX}:\text{XR}$.

When, on the other hand, substances which form conducting solutions are dissolved in water, not only does the compound become hydrolysed with formation of complexes of the type

$RX \begin{smallmatrix} \text{H} \\ \text{OH} \end{smallmatrix}$ (a), but its component groups also become distributed (re-

arranged), forming complexes of the type $H_2O \begin{smallmatrix} \text{R} \\ \text{X} \end{smallmatrix}$ (b); the latter process is a kind of hydrolysis, but the groups are only distributed and not set free. The occurrence of electrolysis in such solutions is dependent on influences which the composite molecules (a and b) exert reciprocally on one another whilst under the influence of the electric strain.

The above considerations are applied to the interpretation of the most various properties of aqueous solutions, such as electrolytic conductivity, hydrolysis, neutralisation of acids by alkalis, hydration, compressibility, and the so-called ionic properties of aqueous solutions. It is considered that the conductivity in concentrated solutions is conditioned mainly by molecules of the hydrolysed solute of type b, whilst in dilute solutions it is due mainly to molecules of type a. In general, the changes which take place in aqueous solution involve the interaction of the composite molecules above referred to; for example, the neutralisation of hydrochloric acid by sodium hydroxide may be represented by the equation:



The considerable expansion attending such neutralisations cannot be adequately accounted for on the ionic theory, but on the present theory, is a simple consequence of the different modes of combination of the water before and after neutralisation. It is shown that when measurements are made with weight-normal solutions, the change of volume on neutralisation is greater for sodium than for potassium salts.

Hydration may be of two kinds, according as it involves hydrolyation or hydronation. The effect of sugars in reducing the conductivity of electrolytes (compare No. X) is probably connected with the association of their oxygen atoms with hydrol. In hydrones, for example, $NaCl \cdot OH_2$, the salt is rendered comparatively inactive, but, owing to the ethenoid linking, the associated water has probably a greater optical effect than ordinary water, the increase in refractive index which attends solution in water being thus accounted for.

G. S.

Studies of the Processes Operative in Solutions. VII. Relative Efficiencies of Acids as Deduced from their Conductivities and Hydrolytic Activities. HENRY E. ARMSTRONG and E. WHEELER (*Proc. Roy. Soc.*, 1908, 81, 1, 95-102).—The electrolytic and hydrolytic activities of hydrochloric, nitric, and sulphuric acids in various dilutions are contrasted, and the conclusion is drawn that the processes are altogether different in character. The hydrolytic activity was determined with sucrose in the usual way, and weight-normal solutions were employed.

When weight-molar solutions of the three acids are compared

nitric acid is least, and sulphuric acid most, active as hydrolyst, and to reduce the other acids to the same activity as nitric acid, 3 mols. of water have to be added to the hydrochloric acid solution and 7 mols. to the sulphuric acid solution. In 1/10 and 1/20 molar solution, hydrochloric and nitric acids are more nearly equal in activity, but sulphuric acid is much stronger than either, its strength not being reduced so much by dilution. The diminution of hydrolytic activity on dilution from molar to 1/10 molar solution for the monobasic acids is not proportional to the dilution, but about 1.5 times as great.

For solutions of the three acids of equal conducting power, the hydrolytic activities at 25° are in the ratio $\text{HNO}_3 : \text{HCl} : \text{H}_2\text{SO}_4 = 100 : 107 : 180$ when the activity of weight-normal nitric acid ≈ 100 .

The molecular conductivities of the various solutions are also given in tabular form.

G. S.

Studies of the Processes Operative in Solutions. VIII. The Influence of Salts on Hydrolysis and the Determination of Hydration Values. HENRY E. ARMSTRONG and D. CROTHERS (*Proc. Roy. Soc.*, 1908, 81, A, 102—112. Compare Senter, *Trans.*, 1907, 91, 460; *Proc.*, 1908, 24, 89).—It has been shown in a previous paper (No. IV, *loc. cit.*) that the "average degree of hydration" of certain alkali chlorides and nitrates is considerably greater when determined from hydrolysis experiments with sucrose in the presence of the corresponding acids than when methyl acetate is used as hydrolyte, and that the nitrates give lower values than the chlorides, especially with methyl acetate. On the preliminary assumption that the results obtained with sucrose are the true hydration values, and that the smaller values observed with methyl acetate are due to combination of salt and ester, the average amount of each salt combined with the ester is calculated. This explanation of the different effect on the two hydrolytes is not, however, regarded as satisfactory.

In order to obtain further information on this point, the relative influence of nitrates and chlorides on the molecular solution volume of methyl acetate, and on the electrical conductivities of the respective acids in the presence and absence of methyl acetate, has been measured, but in no case is the difference so great as for the influence on the hydrolytic activity. For comparative purposes, the effect of sucrose, dextrose, and raffinose on the conductivity of the salts was also measured.

It is suggested that the differences are best accounted for on the basis of the considerations advanced in communication VI. The "hydration values" will vary from case to case, and the highest values will be obtained by using hydrolytes and hydrolysts which form relatively stable hydrols in solution, as these will be less affected by the introduction of salts. Methyl acetate holds hydrol but weakly, and is therefore easily rendered inactive by salts.

The effect of methyl acetate in diminishing the conductivity of electrolytes is probably mainly mechanical, but the sugars appear to exercise a direct dehydrating influence as well as a mechanical effect.

G. S.

Studies of the Processes Operative in Solution. IX. Determination of Optical Rotatory Power. ROBERT J. CALDWELL and R. WHYMPER (*Proc. Roy. Soc.*, 1908, 81, 4, 112—117).—A modified polarimeter provided with a spectroscopic eyepiece is described and figured. A sodium lamp for obtaining a very bright flame is described, but the Bastian mercury lamp was found to possess considerable advantages as a source of illumination, the green line ($546.1 \mu\mu$) being, very bright, pure, and of constant intensity. G. S.

Studies of the Processes Operative in Solutions. X. Changes Effected by the Reciprocal Interference of Sucrose and other Substances (Salts and Non-electrolytes). ROBERT J. CALDWELL and R. WHYMPER (*Proc. Roy. Soc.*, 1908, 81, 4, 117—140).—The effect on rotatory power, the volume change, and (in the case of salts) the change of conductivity produced by adding sucrose to each of a large number of electrolytes and non-electrolytes in weight-molar solution, have been determined.

The influence of non-electrolytes on the rotatory power is slight; the greatest effect is exerted by acetaldehyde (an increase) and by chloral hydrate (a decrease). Electrolytes all diminish the rotation slightly, and the effect increases in the order nitrates, chlorides, sulphates, alkali hydroxides; it is ascribed mainly to combination between electrolyte and sugar.

The molecular conductivity of the most various salts (in molar solution) is reduced to the extent of 43—51%, by the addition of 1 mol. of sucrose. The diminution is partly due to combination between sugar and salt, but mainly to the reduction of the salt to an inactive state, probably by withdrawal of hydrol (compare No. VI). On the basis of certain assumptions, an attempt has been made to ascertain the extent to which sugar enters into combination with certain salts. The order of the effect of salts on the rotatory power is in the main the same as that in which their conductivity is affected by the addition of sugar.

The admixture of sugar with salts in solution is usually attended with considerable expansion, but in the case of non-electrolytes there is very little effect. G. S.

Calculation of the Diffusion Constants of Non-electrolytes in Solution. MAX VON WOGAT (*Ber. deut. physikal. Ges.*, 1908, 6, 542—545).—By means of the author's formula (*Anstr.*, 1907, ii. 606) for the diffusion constant of a non-dissociated substance in dilute solution, values are obtained for aqueous solutions in approximate agreement with the experimental values. The values for the diffusion constants of bromine and ioline in benzene and carbon disulphide do not agree so well with the observed values, and this is attributed to the relatively larger size of the solvent molecules. H. M. D.

Theory of Capillarity. E. T. WHITTAKER (*Proc. Roy. Soc.*, 1908, 81, 4, 21—25).—The surface energy, λ of a liquid is related to the surface tension, γ , by the equation: $\gamma = \lambda + T.d\gamma/dT$, where T denotes absolute temperature. By means of this equation, the surface energy

for a few non-associating liquids has been calculated from the values of the surface tension at different temperatures observed by Ramsay and Shields, and it is then shown that the surface energy of a liquid in contact with its own vapour at any temperature is proportional to the product of the "internal latent heat" and the absolute temperature. The "internal latent heat" is that part of the observed latent heat which is used up in increasing the internal energy of a substance as it passes from the state of liquid to that of vapour.

G. S.

Viscosity of Colloidal Silver Solutions. H. W. WOODSTRA (*Zeitsch. physikal. Chem.*, 1908, 63, 619—622. Compare this vol., ii, 160).—The viscosity of a given colloidal silver solution gradually diminishes with time. When solutions containing different amounts of silver are compared, it is found that the viscosity increases with the concentration. The viscosity of a colloidal silver solution is lowered by electrolytes, an observation which should be contrasted with the action of electrolytes on gelatin solutions (see, for instance, Levites, this vol., ii, 161).

J. C. P.

The "Negative" Viscosity of Aqueous Solutions. WILLIAM WHITE TAYLOR and T. W. MOORE (*Proc. Roy. Soc. Edin.*, 1908, 27, 461—471. Compare Taylor and Ranken, *Trans. Roy. Soc. Edin.*, 1906, 45, 397; Jones and Veazey, *Abstr.*, 1907, ii, 438; Getman, *ibid.*, ii, 744).—In order to test the theory that the cations, in opposition to undissociated molecules and anions, tend to diminish the viscosity of water, and that the activity of the cations increases in general with the atomic volume, the authors have measured the viscosity of aqueous solutions of tetramethylammonium iodide, tetraethylammonium chloride and bromide, and of tetrapropylammonium chloride and iodide at 25° and 35°.

The viscosity increases with increasing volume of the cation, and in no case is there the slightest approach to "negative" viscosity. The influence of the anion on the viscosity is very small. The values for tetraethylammonium chloride and bromide are much more nearly equal than the viscosities of solutions of hydrochloric and hydrobromic acids, of the potassium salts, or of the ammonium salts. The viscosity of salt solutions cannot therefore be regarded as simply an additive property.

The density of tetrapropylammonium chloride solutions decreases with increasing concentration, the diminution being more marked at 35° than at 25°.

H. M. D.

Theory of Adsorption. T. BRAILSFORD ROBERTSON (*Zeitsch. Chem. Ind. Kolloide*, 1908, 3, 49—76).—A theoretical paper of a highly controversial character, in which the view is advocated that the phenomena of adsorption are in reality chemical equilibria, in which capillary condensation plays at most a very unimportant part.

T. E.

Adsorption Phenomena of Inorganic Salts. HANS E. WOHLERS (*Zeitsch. anorg. Chem.*, 1908, 59, 203—212).—When barium sulphate is precipitated in a strong solution of potassium permanganate, the precipitate carries down some of the permanganate, as is shown by the fact that after boiling with hydrochloric acid to remove manganese dioxide the precipitate is still rose-red. The amount of permanganate adsorbed is too small to be estimated gravimetrically. The adsorbed permanganate does not react with hydrogen peroxide or sulphurous acid, nor does adsorbed ferric chloride react with potassium ferrocyanide. On heating the precipitates, however, adsorbed substances undergo chemical changes; thus the pink barium sulphate becomes brown on heating, owing to the formation of manganese peroxide, and adsorbed red cobalt sulphate becomes blue on heating.

Strontium sulphate also adsorbs potassium permanganate, but calcium and lead sulphates and silver chloride do not do so to any appreciable extent.

The absence of chemical reactivity on the part of adsorbed substances might be accounted for on physical lines as being due to a great diminution of solubility, but the author considers it more probable that precipitate and adsorbed substance become chemically combined.

G. S.

Dissociation of a Compound in a State of Equilibrium, and a Thermodynamic Relation Necessary to the Validity of the Law of Constant Proportions. RUDOLF RUER (*Zeitsch. physikal. Chem.*, 1908, 64, 357—373).—It has been shown (Abstr., 1907, ii, 433) that a compound AB fusing to a homogeneous liquid, and capable of dissolving both A and B , must be dissociated when in a state of equilibrium. The conditions of such equilibria in the solid, liquid, and gaseous state are now discussed on the basis of the thermodynamic potential. It is shown on theoretical grounds that two solid or two liquid phases must always possess a certain degree of miscibility, although this miscibility may be very small. C. H. D.

The Unimolecular Course of the Decomposition of Ammonia by the Silent Discharge. ROBERT POHL (*Zeitsch. Elektrochem.*, 1908, 14, 439; MAX LE BLANC, *ibid.*, 507).—A claim for priority against Le Blanc and Davies (this vol., ii, 653) and a reply by Le Blanc, who points out that, whereas Pohl found the decomposition to be unimolecular, he and Davies arrived at the opposite result.

T. E.

Position of the Ammonia Equilibrium. FRITZ HABER and ROBERT LE ROSSIGNOL (*Zeitsch. Elektrochem.*, 1908, 14, 513—514).—In consequence of Jost's criticism (this vol., ii, 761), the authors have made measurements with thermocouples both inside and outside their quartz tube, which show that the difference of temperature is at most 3° . They maintain the accuracy of their results (Abstr., 1907, ii, 454; this vol., ii, 362).

T. E.

Temperature of Dissociation of Ammonia and of Carbon Monoxide. HERMAN C. WOLTERECK (*Compt. rend.*, 1908, 147, 460—461).—Pure dry ammonia was passed through a heated tube of Jena glass. The first signs of dissociation were observed at 620°; above 630° an explosible mixture of gases was produced. Decomposition occurred at a considerably lower temperature in presence of traces of organic matter or water vapour. When passed over heated iron gauze, dissociation commenced at 320°, whilst in presence of ferric oxide no decomposition took place below 420°.

Carbon monoxide dissociates at 570—580°, but in presence of traces of moisture no decomposition occurs even at higher temperatures.

W. O. W.

Theory of Colloids. EDUARD JORDIS (*Zeitsch. Chem. Ind. Kolloide*, 1908, 3, 13—26. Compare this vol., ii, 675).—The suspension theory, the theory of electric charges, the adsorption theory, and the partition theory are criticised, in the sense that none of them is applicable to all colloids, and that they all neglect chemical changes in the colloid itself and reactions between it and substances in solution.

T. E.

Modification of Wolfgang Ostwald's System of Colloids. P. P. VON WEIMARN (*Zeitsch. Chem. Ind. Kolloide*, 1908, 3, 26—27).—In dispersed systems the dispersion may be molecular (as in true solutions of solids or liquids) or the molecules may be aggregated to minute crystals or drops (as in suspensions or emulsions). Between these extremes there are molecular dispersions of compounds of high molecular weight, and then "suspensoids" and "emulsoids" (colloidal solutions in which the colloid is solid or liquid). True solutions are called *dispersions*; colloidal solutions, suspensions, and emulsions are called *dispersoids*. The word colloid is avoided altogether.

T. E.

System of Colloids. WOLFGANG OSTWALD (*Zeitsch. Chem. Ind. Kolloide*, 1908, 3, 28—30).—The nature of gelatin and agar-agar solutions is discussed. The author gives reasons for supposing them to contain two liquid phases; the gelatinous precipitates of inorganic salts obtained by von Weimarn (this vol., ii, 90) are regarded as emulsions of two different solutions, which are prevented from mixing by solid membranes of the salt. A high molecular weight is not a necessary condition for the existence of a substance in the gelatinous form, which appears rather to depend on the physical conditions than on the chemical nature of the substance.

T. E.

Classification of Solutions of Colouring Matters. H. FREUNDLICH and W. NEEMANN (*Zeitsch. Chem. Ind. Kolloide*, 1908, 3, 80—83).—The solutions of colouring matters are true solutions, semi-colloidal and colloidal. They are classified by their diffusion through parchment paper and by their ultra-microscopic behaviour. The colloidal solutions belong to two classes, the suspension colloids, the freezing point and surface tension of which are practically the same as those of pure water, and the emulsion colloids, the properties of which differ from those of water.

Measurements of the surface tension of aqueous and alcoholic solutions of several colouring matters are given. They all form true solutions in alcohol, and the surface tension is slightly increased. Among the aqueous solutions, rhodamine (true solution), crystal-violet (semi-colloidal), and night-blue (colloidal) diminish the surface tension, whereas the other colouring matters leave it practically unchanged.

T. E.

Effect of Electrolytes on the Viscosity of Colloids. GOKUN (*Zeitsch. Chem. Ind. Kolloide*, 1908, 3, 84—88).—The effect of ammonium nitrate on the viscosity of solutions of gelatin is studied. The viscosity of a pure gelatin solution (0.28%) increases with time, increasing by one-half in 115 hours. The addition of ammonium nitrate diminishes the rate of increase, so that when the concentration of the salt is from 1.5*N* to 2*N*, the viscosity remains almost constant; with greater concentrations, the viscosity diminishes with the time instead of increasing. The viscosity depends on the mechanical treatment to which the solution has been subjected; repeated passage of the same solution through a capillary tube gives different results; also, the viscosity measured by passing the solution through a narrow tube under high pressure is not the same as that observed with a wider tube and lower pressure. This points to the existence of a structure in the solutions.

T. E.

Nature of Precipitated Colloids. HARRY W. FOOTE (*J. Amer. Chem. Soc.*, 1908, 30, 1388—1394).—Experiments are described which afford evidence that precipitated ferric and aluminium hydroxides may be regarded as solutions of water in the oxides or lower hydroxides, that is, solutions of liquids in solids.

Samples of the precipitated hydroxides were left in the air for several days at the temperature at which the experiments were to be carried out. The composition of the material was then determined by ignition, and a weighed quantity was put into a porcelain crucible, which was placed on a raised triangle in a large weighing bottle containing a little water. The bottle was carefully sealed and left for eighteen to forty-eight hours. The crucible was then quickly removed, and weighed in order to determine the change of weight. The experiments were made at 25° and 45°. The composition of the product at any point could be calculated from the known composition of the original material.

All the moist precipitates lost weight slightly over water, but, after being dried in the air to a certain point, they began to gain weight when placed over water. This was due to the fact that their vapour pressures had fallen below that of the water, showing that the water phase had just disappeared. The composition at the point at which the gain in weight first occurred was approximately that of the saturated hydrate free from mechanically-contained water. The averages of a large number of determinations gave the following as the composition of the saturated solutions of water in the oxides.
 Ferric hydroxide at 25°: Fe_2O_3 , 47.72—47.79%; at 45°, 54.53—56.74%.
 Aluminium hydroxide at 25°: Al_2O_3 , 49.52—51.17%; at 45°, 52.54—53.82%.

Similar experiments were made with zirconium hydroxide, and the composition of the saturated solutions at 25° were found to be: ZrO_2 , 32.02—32.33%.
F. G.

Coagulation of Colloidal Solutions in Galvanic Cells. WILHELM BILTZ (*Zeitsch. Elektrochem.*, 1908, 14, 567—571).—Two metals are immersed in solutions of colloidal ferric hydroxide, gold, or antimony sulphide, purified by dialysis, and the cell so formed short circuited. In all cases the colloid is coagulated, the precipitate forming partly on one of the metals and partly in the solution near it. The more noble metals alone have no action; the less noble ones have a small action. Ferric hydroxide is precipitated on or near the more noble metal of the couple; gold and antimony sulphide go to the less noble metal. The phenomenon is not due to the current alone; the *E.M.F.* of the zinc copper element, for example, is under 1 volt, and this voltage applied to platinum electrodes in a gold hydrosol produces no precipitate. On the other hand, the quantity of zinc hydroxide which is formed from the zinc electrode is comparable in weight with the quantity of gold precipitated, and it is found almost entirely in the precipitate. The action therefore appears to be mainly due to the action of bivalent ions formed from the metals in the short circuited cells.
T. E.

Agglutination and Coagulation. SVANTE ARRHENIUS (*J. Amer. Chem. Soc.*, 1908, 30, 1382—1388).—The work described was carried out with the object of obtaining evidence as to the nature of agglutination. Two views have been advanced, one, the colloidal theory, according to which the suspended particles (bacteria or blood corpuscles) collect together and subside under the influence of electrolytes or agglutinins, and the other, first proposed by Duclaux, that agglutination depends on the coagulation of some substances in the cells which causes the cells to cling together and subside.

Experiments have been carried out on the precipitation and agglutination of blood corpuscles by means of various salts. Ox-blood corpuscles were suspended in solution of sodium chloride (0.9%) or sucrose (7%), the emulsions containing 4, 1, and 0.25% of corpuscles. To 5 c.c. of such solutions, varying quantities of the salt solutions were added. The minimum quantity of each salt required for precipitation and for agglutination was noted. The results are tabulated, and show that, with certain exceptions, there is a well-marked relation between the precipitating and agglutinating powers of each salt. Salts which give a maximum precipitation at a certain concentration also give a maximum agglutination at a certain concentration, but if a maximum does not appear in the one case, it also fails in the other. It is therefore concluded that, as Duclaux has suggested, agglutination depends on a precipitation, and that this precipitation is due to a chemical reaction between the metal ions and the proteins in the corpuscles. In general, both precipitation and agglutination in sugar solutions require less quantities of the added salt than in sodium chloride solutions.

Many substances cause agglutination as well as hemolysis of the

blood corpuscles, and among these may be mentioned the nitrates of silver and lead, mercuric chloride, and the acids (compare this vol., ii, 708). The hæmolytic action does not run parallel with the agglutinating action.

The quantity of a salt required to be added for the precipitation of a blood solution is proportional to the concentration of the latter. Since the quantity of the salt required increases more slowly than the concentration, it is evident that there exists a chemical equilibrium between the two salt-like products derived from the blood solution and the ions of the precipitating salt. All the evidence obtained in this investigation is in favour of the physico-chemical theory, according to which the observed phenomena are due to ordinary chemical processes.

E. G.

Permeability of Ultra-filters. HEINRICH BECHHOLD (*Zeitsch. physikal. Chem.*, 1908, 64, 328—343).—The author's gelatin "ultra-filters" (this vol., ii, 24), for the separation of colloids from the solvent, vary in fineness according to the concentration of the gelatin. Some of them are too fine to allow of the determination of the size of their pores by ultra-microscopic examination of the colloids retained by them. By considering the pores as capillary tubes or as slots, their dimensions can be arrived at by measuring the pressure required to force air through them when immersed in water. This method was controlled by tests with a filter-paper which retains ox-blood corpuscles (diam. $7-8\mu$), for which the air-pressure method gave an average value of 1.5μ , and with Chamberland porcelain filters, which retain cocci (diam. 1μ), and where the method gave as a result 0.3μ . The same method provides a test for the uniformity in size of the pores. Ultra-filters may be tested in this way, and by the rate of passage of water.

Tests with ultra-filters indicate that the smallest particles of hæmoglobin have one-sixth the diameter of collargol particles, and that the smallest particles of litmus in alkaline solution, or of soap solution, have less than one-half the diameter of hæmoglobin particles.

C. H. D.

Foam Structure [Cellular Structure] of Sulphur and its Influence on Double Refraction, Dichroism, Electrical Properties and Formation of Crystals. GEORG QUINCKE (*Ann. Physik.*, 1908, [iv], 26, 625—711).—A historical account is given of work relating to the different forms which sulphur may assume. The form of the heating and cooling curves of liquid sulphur and the variation of the surface tension with the temperature are also discussed. The micro-structure and the optical properties of the solid products which are obtained by cooling liquid sulphur under different conditions, and also of the products obtained by the condensation of sulphur vapour, have been examined. The conclusions of chief interest are that there are four forms of sulphur, S_a , S_b , S_c , and S_d , which are stable respectively between the limits $0-96^\circ$, $96-160^\circ$, $160-300^\circ$, and $300-448^\circ$; further, that liquid sulphur has a jelly-like cellular structure, and represents a mixture of solutions containing these

allotropic modifications in different proportions, the several solutions being separated by limiting surfaces in which surface-tension forces play an important part. At one and the same temperature, liquid sulphur may contain solutions in which these modifications are present in different proportions, this being determined by the previous physical treatment of the sulphur.

H. M. D.

Velocity of Reaction. JOHANNES J. VAN LAAR (*Chem. Weekblad*, 1908, 5, 698—705).—A theoretical paper, in which the theory of reaction velocity is criticised, and a new thermodynamic theory put forward.

A. J. W.

Temperature-coefficient of the Velocity of Chemical Reactions. I. MAX TRAUTZ and KARL THEODOR VOLKMAN (*Zeitsch. physikal. Chem.*, 1908, 64, 53—88).—The velocity of saponification of eight esters in aqueous solution has been determined over a wide range of temperature. The temperature-coefficient of the velocity rises to a maximum between 10° and 20° in all cases, and thereafter falls off. At 60°, the value of the temperature-coefficient is frequently as low as 1.4, so that the difference in magnitude as compared with the temperature-coefficient of a photochemical reaction is not so marked as has usually been assumed. The existence of a maximum temperature-coefficient between 10° and 20° is probably connected with an irregularity which occurs in the viscosity of water in that region. The observed variation of the temperature-coefficient with the temperature may in fact be reproduced by a formula into which the viscosity of water enters.

The authors' experiments tend to show that the mass action law is strictly applicable to the saponification of esters only when the concentration is less than $N/5$.

The paper contains an extensive list of references to earlier papers on the temperature-coefficient of reaction velocity, and this earlier work is subjected to a critical review.

J. C. P.

The Dynamic Theory of a Reversible Chemical Reaction. ERNST COHEN and TH. STRENGERS (*Chem. Weekblad*, 1908, 5, 594—595. Compare Smits and Wibaut, *Proc. K. Akad. Wetensch. Amsterdam*, 1908, 11, 114).—Arguments are adduced to prove that the transformation $2CO \rightleftharpoons CO_2 + C$ is not an experimental proof of the truth of the dynamic theory of reversible reactions.

A. J. W.

The Dynamic Theory of a Reversible Chemical Reaction. ANDREAS SMITS and J. P. WIBAUT (*Chem. Weekblad*, 1908, 5, 625—626; *Proc. K. Akad. Wetensch. Amsterdam*, 1908, 11, 162—164).—Polemical. A reply to Cohen and Strengers (preceding abstract).

A. J. W.

Effect of Ferric Salts on the Rate of Oxidation of Ferrous Salts and on the Catalytic Action of the Latter. W. F. GREEN (*J. Physical Chem.*, 1908, 12, 389—397).—The influence of ferric salts on the rate of oxidation of ferrous salts by chloric acid and by oxygen, and on the rate of oxidation of iodides

by chloric and bromic acids in the presence of ferrous salts, has been investigated. It is found that ferric salts are without influence on the rate of oxidation of ferrous salts by chloric acid and by oxygen. The liberation of iodine from iodides by chloric and bromic acids is accelerated by both ferrous and ferric salts, the rate depending merely on the amount of iron present, and not on its state of oxidation. In solutions containing ferrous and ferric salts, the effects of the two are additive.

H. M. D.

Reaction between Potassium Ferricyanide and Potassium Iodide. GERHARD JUST (*Zeitsch. physikal. Chem.*, 1908, **63**, 513-578. Compare Donnan and Le Rossignol, *Trans.*, 1903, **83**, 703).—This reaction may be conceived as involving two stages: (1) $\text{FeCy}_6''' + \ominus = \text{FeCy}_6''$; (2) $\text{I} + \oplus = \text{I}$. The velocity of the latter process is practically that of an instantaneous reaction, as shown by Brunner (*Abstr.*, 1907, ii, 223). Process (1), however, is not to be regarded as an instantaneous reaction, as shown by a study of the polarisation at an electrode immersed in a solution containing both ferro- and ferri-cyanide. When the electrode consists of platinum, it is practically unpolarisable, but this is not at all the case when the electrode consists of gold or silver. Hence process (1) is not instantaneous; it is very markedly accelerated by platinum, the acceleration being apparently connected with an oxidation and reduction of the metal. The accelerating effect of platinum on the rate of reaction between potassium ferricyanide and iodide can be demonstrated directly. From the fact that process (1) is not instantaneous, the author draws the conclusion that the difference between the FeCy_6''' and FeCy_6'' groups cannot be one of charge alone; they must have a different constitution.

The results of quantitative experiments made on the rate of reaction between ferricyanide and iodide confirm those recorded by Donnan and Le Rossignol (*loc. cit.*), but the interpretation of the results is different. The application of the Noyes-van't Hoff formula to the author's measurements shows that the reaction is of the first order in regard to the ferricyanide, and of the second order in regard to the iodide. Altogether, therefore, the reaction between potassium ferricyanide and iodide is one of the third order, not of the fifth, as held by Donnan and Le Rossignol.

It appears fairly certain that it is the undissociated ferricyanide which takes part in the reaction, for the velocity is very markedly increased by the addition of indifferent potassium salts. In what form the iodide takes part, whether as ion or as undissociated salt, it is not possible to determine, although it is considered most probable that the ions are actively concerned.

A complete kinetic equation has not been constructed, but attention is drawn to the following observations, which would have to be considered in working out such an equation. The reaction between ferricyanide and iodide is notably retarded by ferrocyanide, but not by iodine; it is accelerated by both cyanide and thiocyanide ions; it is retarded by hydroxyl ions, but accelerated by hydrogen ions. Indications were also obtained that an intermediate product plays some part in the reaction.

J. C. P.

Are the Stoichiometric Laws Intelligible without the Atomic Hypothesis? OTTO KUHN (*Chem. Zeit.*, 1908, 32, 767-769. Compare Abstr., 1907, ii, 678; this vol., ii, 98).—A further adverse criticism of the papers by Wald (Abstr., 1907, ii, 755; this vol., ii, 367). J. V. E.

Laboratory Apparatus. • W. HEBER GREEN (*Chem. News*, 1908, 98, 49-50).—*Determination of Density.*—The maximum error liable to occur in determining the density of water by means of a pear-shaped specific gravity bottle is found to be 0.00002. To obtain this accuracy, the bottle, which can only be used for temperatures above that of the surrounding atmosphere, is filled with the solution and immersed to the neck in a thermostat constant within 0.04; after ten to fifteen minutes, the expansion of the solution through the perforated stopper is complete; the bottle is then dried and cooled for fifteen minutes, and finally weighed, the density being calculated from the formula $d = M/W(1 + 0.0012/d - 0.0012)$, in which W and M are the apparent weights of water and solution respectively required to fill the bottle. The formula is only approximate, and disregards variations of atmospheric pressure which are often sufficient to nullify the correction. The most serious fault of the instrument is the fact that wear on the ground surfaces of the stopper and neck diminishes the capacity of the pycnometer.

A Sensitive Form of Thermo-regulator.—The thermostat is of the ordinary type, and consists of a toluene bulb of about 20 c.c. capacity attached to a U-tube containing mercury, which is connected by a capillary tube to the by-pass, the novelty of which is that the gas inlet-tube is slightly opened out instead of being left square. As soon as the mercury reaches the funnel-shaped opening of this tube, its capillarity tends to force it down again and so admit the gas supply. The temperature was found to remain constant within 0.01 for several weeks, provided the bath was efficiently stirred.

A Sensitive Temperature-compensated Barometer.—A modification of a Huyghens glycerol-mercury barometer in which the former liquid is replaced by paraffin oil, b. p. 236°. The vapour pressure of this oil varies with temperature at such a rate as almost exactly to neutralise the effects of the accompanying expansion of mercury for the particular dimensions of tubes used. The rise and fall of the liquid for a variation of one-hundredth of an inch in the atmospheric pressure is sufficiently large to be seen at some distance. P. H.

Erper's Gas Generating Apparatus. 1. GUTMANN (*Zeitsch. angew. Chem.*, 1908, 21, 1798).—The apparatus consists of a pear-shaped funnel for holding marble or iron sulphide, which is fitted into the neck of a bottle containing acid; the lower end of the bottle is connected by a side-tube and a tap, A, to a raised reservoir. The top of the funnel is fitted with a tap, B, and a delivery tube, near the lower end of the funnel is a side-tube through which the spent acid may be withdrawn after closing the delivery tube and opening the tap B. When re-charging with solid, the tap A is closed. P. H.

Modified Form of Saint-Claire Deville's Apparatus for Continuous Production of Gases. VICTOR GRIGNARD (*Bull. Soc. chim.*, 1908, [iv], 3, 890—892).—The modification is devised to overcome the disadvantages of the ordinary Saint-Claire Deville apparatus, namely, the difficulty of using up the whole of the acid and the clogging of the rubber tubing by crystals deposited from the saturated solutions formed when the apparatus has been long in action.

For this purpose, the ordinary rubber tube connexion is prolonged upwards at an obtuse angle inside the bottle containing the acid, by a glass tube reaching to a level slightly below that of the liquid, so that it is always the strongest acid which comes into action first, and the denser liquid remains at the bottom of the bottle. Continuity of action can be secured by having the side aperture of the acid bottle halfway up the latter, and making the connexion between the two bottles by two glass tubes parallel to each other and prolonged into the acid bottle at obtuse angles to the horizontal with their arms turned in opposite directions. To permit of this arrangement, the bottle containing the solid is raised on a small block, so that its side aperture is opposite that of the acid bottle. In this way by the action of gravity a continuous flow of acid through the solid to be acted on is maintained.

T. A. H.

Simple Regulator for High Pressure Gas. ROBERT LE ROSSIGNOL (*Chem. Zeit.*, 1908, 32, 820).—By making the cone angle of an ordinary screw-down tap very small (4°), it is possible to obtain gas from a cylinder at any required pressure in a simple manner. A slow, steady current of oxygen, as used for combustion purposes, may be obtained directly from a cylinder of the compressed gas by using such a form of tap.

J. V. E.

New Method for Calibrating Capillary Tubes. BOHDAN VON SZYSZKOWSKI (*Zeitsch. physikal. Chem.*, 1904, 64, 201—214).—The process and apparatus are practically the same as those employed in the measurement of surface tension. The heights to which water and dilute solutions of isobutyric acid rise in two capillary tubes of about the same bore are accurately measured, and the exact radius of the tubes at various points is thus determined. The application of the method is illustrated by full data for two tubes which the author has examined.

J. C. P.

Improved Pipette. WORTHIE (*Chem. Zentr.*, 1908, ii, 1; from *Arch. Kais. Gesundheits-Amt.*, 1908, 28, 401—404).—This suction arrangement for use with very poisonous or infectious materials consists of a small syringe of about 5 to 7 ccm. capacity, connected to a pipette by a U tube, and held by a spring clip.

J. V. E.

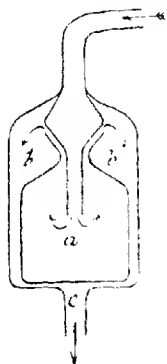
Automatic Syphon Pipette. HERRERT S. BAILEY (*J. Amer. Chem. Soc.*, 1908, 30, 1508—1509).—A description and diagram are given of an apparatus for delivering approximately constant quantities of a reagent, such as the sulphuric acid for the Babcock milk test or

the Kjeldahl nitrogen estimation. For details, the original must be consulted.
E. G.

Steam Inlet-tube. H. STOLTZENBERG (*Chem. Zeit.*, 1908, 32, 770).—Instead of the ordinary open inlet-tube used for steam distillation purposes, a tube is described which is closed at the lower end, the steam being allowed to enter the liquid from a number of short, horizontally-curved side-tubes placed near the end. By this means the distillation flask may be used in an upright position; bumping is avoided because the liquid is caused to rotate rapidly by the issuing steam, and the process of distillation is considerably hastened.

J. V. E.

New Safety Valve. H. STOLTZENBERG (*Chem. Zeit.*, 1908, 32, 832).—A safety valve is described for use when gases are to be absorbed in liquids, such as carbon dioxide in potash solution. It will



be seen from the figure, that the gas after entering *a*, passes between the open ground-glass joint into the outer vessel *b*, and then through *c* to the potash solution. Should the absorption be so rapid as to cause the potash solution to flow back, the small inner flask is lifted up and closes the joint connecting *a* with *b*.

J. V. E.

Use of Electrical Heating in Fractional Distillation. THEODORE W. RICHARDS and J. HOWARD MATHEWS (*J. Amer. Chem. Soc.*, 1908, 30, 1282—1284; *Zeitsch. physikal. Chem.*, 1908, 64, 120—123).—In determining the latent heat of vaporisation of certain substances by a modification of Kahlenberg's method, it was observed that each organic liquid boiled much more constantly when heated electrically by the platinum

coil immersed in it than when distilled in the ordinary way. A special form of apparatus has therefore been devised for use in fractionating organic liquids.

At the bottom of an ordinary stout distilling flask, a depression is blown of about the same diameter as the neck of the flask, and into this is placed a coil consisting of about 40 cm. of platinum wire with a resistance of about 0.7 ohm. A current of 10—15 amperes is led to the resistance coil from above by heavy copper wires of 2.5—3.0 mm. diameter enclosed in glass tubes, into the ends of which the ends of the platinum wire are sealed, contact being made by a drop of mercury.

Since the bubbles of vapour arise only from the small area of the resistance coil, ebullition proceeds quietly and without any bumping. The method is especially applicable to fractional distillation under reduced pressure; it obviates superheating, and effects a much more rapid and complete separation than the ordinary method of distillation.

E. G.

Receiver for Vacuum Fractional Distillation. J. FREUNDLICH (*Chem. Zeit.*, 1908, 32, 820).—An arrangement is described for collecting fractions in a vacuum without interrupting the process of distillation, the end of the condenser tube communicating by means of taps and short side-arms with two glass cylinders, the upper ends of which communicate with the exhaust tube by means of taps. J. V. E.

Apparatus for the Rapid Distillation of Mercury. FORTUNATO FLORIO (*Nuovo Cim.*, 1908, [v], 16, 93—96).—An apparatus is figured and described, by which 2·5 kilos. of mercury can be distilled per hour. G. B.

Inorganic Chemistry.

A New Method for the Preparation of Pure Hydrogen. MAURICHAU-BEAUPRÉ (*Compt. rend.*, 1908, 147, 310—311).—Aluminium filings are mixed with a small quantity of mercuric chloride and potassium cyanide in powder. The product, to which the name "hydrogenite" is given, has $D = 1\cdot42$. It can be preserved indefinitely if kept in a dry atmosphere, but when treated with water it becomes oxidised, with development of heat and liberation of pure hydrogen. One kilogram of the powder yields 1300 litres of hydrogen at 15° and 760 mm. To obtain the best yield, the action of the water must be regulated so as to maintain the temperature at about 70°, and a large excess of water should be avoided. W. O. W.

Preparation of Hydrogen Peroxide. C. A. F. KAHLBAUM (D.R. P. 197023).—Hydrogen peroxide can be prepared from its elements, or from a mixture of steam and these elements, or even from steam alone, when these gases are passed through a source of heat with a velocity of not less than one metre per second. The source of heat may be an electric arc, a spark discharge, or a flame of burning hydrogen, and the gases may be kept stationary while the heating apparatus is rotated. On condensing the steam, the hydrogen peroxide is obtained in the form of an aqueous solution. G. T. M.

Production of Hydrogen Peroxide from Aluminium and Zinc. HOWARD T. BARNES and G. W. SHEARER (*J. Physical Chem.*, 1908, 12, 468).—The statement made previously (this vol. ii, 344), that zinc in contact with water containing air or oxygen does not produce hydrogen peroxide, is contradicted by later observations. The difference between the behaviour of zinc and aluminium is traced to the fact that hydrogen peroxide is decomposed fairly rapidly in contact with zinc, but only slowly, if at all, in contact with aluminium. This is probably due to the difference in the extent to which the covering surface films protect the hydrogen peroxide from the action of the metals.

Copper, platinum, and iron in similar circumstances do not yield hydrogen peroxide. H. M. D.

Preparation of Perhydroxide Bases and their Salts. RICHARD WOLFFENSTEIN (D.R.P. 196369).—Sodium perhydroxide, NaOOH , is precipitated by adding 30% hydrogen peroxide to alcoholic sodium hydroxide or ethoxide; it is a strongly basic substance, and, when saturated with carbon dioxide, forms sodium hydrogen percarbonate, NaHCO_4 . This compound is more stable than the product obtained by Tafel from sodium peroxide and alcohol (Abstr., 1894, ii, 448). G. T. M.

Sulphur Anion and Complex Sulphur Anions. JOSEPH KNOX (*Trans. Faraday Soc.*, 1908, 4, 29—49).—Many of the results given in the present paper have already been published (Abstr., 1906, ii, 608). The predominant complex in the solution of mercuric sulphide in sodium sulphide is Na_2HgS_2 , but, when a solution saturated with both sulphides is concentrated over sulphuric acid, a double sulphide of mercury and sodium, $2\text{Na}_2\text{S}_2\cdot 5\text{HgS}_2\cdot 3\text{H}_2\text{O}$, separates in yellow crystals.

The solubility of mercuric sulphide (black and red) in potassium sulphide solutions is somewhat greater than in sodium sulphide; the solubility in equivalent dilute solutions of barium and sodium sulphide is practically equal. The solubility of mercuric sulphide in sodium disulphide, Na_2S_2 , is about half that in the normal sulphide, and in this case, also, the solubility is increased by the addition of sodium hydroxide. From the results of *E.M.F.* measurements, it is probable that the complex anion present in greatest amount is HgS_2^{2-} in this case also.

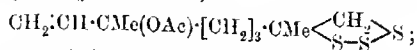
The solubility product $S=[\text{Hg}^{++}][\text{S}^{2-}]$ only remains constant for different ionic concentrations when it is assumed that the hydrolysis of sodium sulphide in dilute (0.05 molar) solution is practically complete. Küster and Heberlein (Abstr., 1905, ii, 155), however, found for the same solution a value less than 90% by a method depending on the decomposition of diacetylacetone. The author has repeated these measurements, and finds a greater degree of hydrolysis than Küster, a result which is confirmed by conductivity measurements.

The solubility products of certain sulphides have been determined by *E.M.F.* measurements with rods of the respective metals dipping in a solution of sodium sulphide. The results at 25° are as follows: $[\text{Ag}^{+}][\text{S}^{2-}]=3.0 \times 10^{-12}$; $[\text{Pb}^{++}][\text{S}^{2-}]=2.6 \times 10^{-13}$, and $(\text{Cu}^{++})[\text{S}^{2-}]=1.2 \times 10^{-12}$. G. S.

Thiozonides. Sulphur and its Cyclic Compounds. HERSCHELMANN and ROCHE (*Annalen*, 1908, 362, 133—173).—Hoffmann and Roche have shown (Abstr., 1906, ii, 279) that molten sulphur cooled to 160° separates into two distinct liquid layers. The new modification of sulphur, which according to Smith and Holmes (Abstr., 1902, ii, 650) must be represented by S_8 , is shown to be S_8 ; in fact, this highly reactive, labile, dark-coloured form of sulphur is the analogue of

ozone, and is consequently named *thiozone*. As it would be more difficult to isolate thiozone in a pure state than ozone, it is best identified by its action on organic compounds. Ozone acts on unsaturated compounds, yielding ozonides or polyozonides (compare Harries, Abstr., 1906, i, 225); similarly, when unsaturated compounds are heated with sulphur at 160°, thiozonides or polythiozonides are formed: $CR_1R_2:CR_3R_4 + S:S:S \rightarrow \begin{matrix} CR_1R_2:S \\ | \\ CR_3R_4:S \end{matrix} > S$.

Terpene Derivatives.—Linalyl acetate is practically unattacked by sulphur at 150°, but at 160° the two substances interact energetically, yielding a *thiozonide*,



the same compound is formed whether the quantity of sulphur employed is very small or greatly in excess of that required to form the monothiozonide; the acetyl group appears to protect the second ethylene linking from the action of thiozone. The thiozonide forms a dark brown, viscid syrup, D₂₀ 1.133, and has a characteristic odour. It absorbs oxygen very rapidly, and reacts both as a thio-acid and thio-base; although insoluble in alcohol, it readily dissolves in an alcoholic solution of sodium sulphide, forming a dark brown solution which contains the sodium salt, C₁₂O₂O₂S₄Na₂; this could not, however, be isolated. The thiozonide yields characteristic precipitates with the chlorides of antimony, arsenic, bismuth, and mercury. An ethereal solution of the thiozonide and auric chloride liberates hydrogen chloride on evaporation, leaving a brown, tarry residue of a gold compound, which, when heated on porcelain, leaves behind a brilliant, coherent coating of gold. The gold compound is also formed by the interaction of the thiozonide dissolved in ethyl acetate with gold sulphide.

Linalool dithiozonide is prepared by heating linalool with sulphur at 160°; hydrogen sulphide is evolved during the reaction, and the brown, viscid mass obtained has the approximate composition C₁₆H₁₆OS₅.

With the object of ascertaining whether linalool and linalyl acetate behave in a similar manner towards ozone, equimolecular solutions of the two substances in carbon tetrachloride were added to equal volumes of a solution of ozone in carbonyl chloride at -70° until the blue colour of the ozone had disappeared. It was found that the same quantity of ozone required twice as much linalyl acetate as linalool, so that the former evidently forms a mono-, whilst the latter forms a di-ozonide.

Sulphur Dyes as Derivatives of Thiozone.—This part of the paper is of a somewhat technical nature. Evidence is advanced which shows that the various sulphur dyes first formed by heating many organic compounds with sulphur and sodium sulphide are thiozonides; for example, like thiozonides, they are insoluble in most solvents, soluble in alkali sulphides, and are readily oxidised by the oxygen of the air at the ordinary temperature. The fact that most sulphur dyes are oxidised by atmospheric oxygen with the liberation of sulphuric acid, and yield hydrogen sulphide when reduced, is readily explained on the

assumption that they are thiozonides containing the chromophoric group $\begin{array}{c} \text{C:S} \\ \text{C:S} \end{array} \text{>S}$. Ris's conclusion (Abstr., 1900, i, 419), that the sulphur liberated as hydrogen sulphide is attached to nitrogen, is very improbable.

Theory of Inorganic Polysulphides.—Although sulphur does not readily act on organic substances below 160° , yet, in the presence of sodium sulphide, action takes place at a much lower temperature. It is therefore probable that the polysulphides are closely related to thiozone. The results of work not yet published show that the alkali metals behave towards sulphur like rubidium towards oxygen (compare Erdmann and Köthner, Abstr., 1897, ii, 96); in fact, the yellow disulphide, NaS_2 , corresponds with the brown oxide, RbO_2 . This disulphide may be represented as a thiozonate, $\text{NaS} \text{>} \text{S} \text{<} \text{S}$, that is, as an additive product of the monosulphide with thiozone. Such thiozonates are among the best characterised polysulphides of the alkali metals; thus, Böttger has shown (Abstr., 1884, 1260) that alkali thiozonates containing varying, yet definite, amounts of water crystallise from solutions of polysulphides containing more or less sulphur; further, the various polysulphides, Na_4S_6 , Na_2S_3 , Na_2S_4 (compare Bloxam, Trans., 1900, 77, 753), when heated at 800° , yield the thiozonate, Na_2S_4 . The fact that pure sulphur dyes are formed by acting on amino-phenols with an alcoholic solution of sodium thiozonate, may be explained by assuming that the thiozonate partly dissociates when its alcoholic solution is warmed, yielding thiozone, $\text{Na}_2\text{S}_4 \rightarrow \text{Na}_2\text{S} + \text{S}_2$, which, in the nascent state, readily unites with the amino-phenol.

Constitution of Ultramarine.—Hoffmann's conclusion (Abstr., 1879, 108), that the sulphur in ultramarine-blue is present in a similar state of combination as in the polysulphide, Na_2S_2 (sodium thiozonate), cannot be correct, since it does not yield silver sulphide with silver nitrate, but is converted into silver ultramarine, in which sodium is replaced by its equivalent of silver (compare Heumann, Abstr., 1880, 217, 367; 1881, 351). Instead, the ultramarines are to be regarded as thiozonides. Hoffmann has shown that white ultramarine, $\text{Na}_{12}\text{Al}_6\text{S}_3\text{Si}_6\text{O}_{24}$, is converted on oxidation into green, and then into blue, ultramarine, both of which also contain the three atoms of sulphur in the molecule. In strict analogy with the ultramarines, sulphur dyes are reduced by powerful reducing agents to leuco-compounds, corresponding with the white ultramarine, which are readily oxidised back to the original dye.

Chemistry of Molten Sulphur.—As has been shown, molten sulphur at 160° contains thiozone; now this substance, like sulphur dioxide, has the character of an acid anhydride, and is consequently able to bring about polymerisation of eight-membered rings (compare Harries, this vol., i, 234). Now ordinary sulphur contains eight atoms in the molecule; consequently, sulphur at 160° probably consists of thiozone, which imparts to the mass its dark colour, together with amorphous sulphur, $(\text{S}_8)_n$, which renders the mass viscid.

Constitution of Polymeric Forms of Oxygen.—Since sulphur exists

as S_8 , it is not improbable that oxygen might also exist in the polymerised form, O_8 . Ladenburg and Lehmann (Abstr., 1906, ii, 509) appear to have obtained evidence of the existence of a highly polymerised form of oxygen, but Warburg and Leithäuser (Abstr., 1907, ii, 342) have thrown doubt on their results. However, it is not improbable that the octa-sulphates described by Weber (Abstr., 1885, 121) contain the eight-membered ring:

$$\begin{array}{c} \text{O} \cdot \text{O} \cdot \text{O} \cdot \text{O} \\ | \quad | \quad | \quad | \\ \text{O} \cdot \text{O} \cdot \text{O} \cdot \text{O} \end{array}$$

Theory of Vulcanised Caoutchouc.—In the vulcanisation of caoutchouc, it is probable that the sulphur liberates thiozone, which forms a thiozonide, and that the viscid, amorphous form of sulphur, $(S_8)_x$, produced simultaneously, forms a semi-solid solution with the caoutchouc, which has a similar constitution to the viscid, amorphous form of sulphur, being a polymerised form of a dimethylcyclooctadiene (compare Harries, *loc. cit.*). Vulcanised caoutchouc is thus a semi-solid solution of polymerised sulphur, $(S_8)_x$, in polymerised dimethylcyclooctadiene, $(C_8H_{10}Me_2)_x$, and its thiozonide. Ebonite is probably a polythiozonide of caoutchouc.

W. H. G.

Selenium and Iodine. GIOVANNI PELLINI and S. PEDRINA (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 78—81).—From a study of the melting-point curve for mixtures of selenium and iodine, the authors conclude that these elements form no compound and no mixed crystals, except within very narrow limits. The eutectic mixture melts at 58° , and corresponds almost exactly with the supposed compound, Se_2I_2 . The identical products obtained in various ways by Schneider (*Pogg. Annalen*, 1866, 129, 627) must be regarded as mixtures of definite composition.

T. H. P.

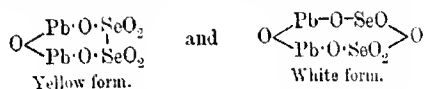
Electrolytic Formation of Selenic Acid from Lead Selenate. FRANK CERRY MATHERS (*J. Amer. Chem. Soc.*, 1908, 30, 1374—1378).—A study has been made of the best conditions for converting lead selenate into lead and selenic acid by electrolysis. The lead selenate is placed in a platinum dish, which serves as the cathode, and a coil of platinum wire is used as the anode. Some reduction products of selenic acid are formed during the process, but these are insoluble and can be removed by filtration. The best efficiency yield, 87%, was obtained at the ordinary temperature, with a low current density at the cathode and a thin layer of lead selenate. The best current yield, 13%, was obtained at 85° , with a low current density and a large amount of lead selenate on the cathode. Selenic acid is only produced in small quantities from lead selenate in contact with the anode.

E. G.

Structural Isomerism. Preparation of Asymmetric Selenites. LUIGI MARINO (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 858—866; *Zeitsch. anorg. Chem.*, 1908, 59, 150—160).—If the author's views concerning sulphurous acid (this vol. ii, 106) hold also for selenious acid, it should be possible to obtain asymmetric selenites. To investigate this question, the action of selenious acid on lead peroxide has been studied. In this way, besides ordinary lead selenite,

a salt, $\text{Pb}_2\text{Se}_2\text{O}_7$, has been obtained as a sulphur-yellow, crystalline powder. When treated with potassium carbonate solution, this salt yields 1 mol. of lead peroxide and 1 mol. of lead oxide per mol., whilst the addition of dilute nitric acid to a solution of the salt in 15% sodium hydroxide solution precipitates the sesquioxide, thus: $\text{Pb}_2\text{Se}_2\text{O}_7 = \text{Pb}_2\text{O}_3 + 2\text{SeO}_2$. When heated at 200° , the yellow salt gradually changes into a white isomeride, exhibiting different reactions from the yellow form; for example, it does not yield lead peroxide when boiled with alkali carbonate solutions. When heated at $40-50^\circ$ with dilute sulphuric acid and potassium permanganate, the white isomeride absorbs 1 atom of oxygen per mol.; under the same conditions, the yellow form is stable, but after long heating to 80° it absorbs 2 atoms of oxygen per molecule.

On the basis of these results, the author proposes the constitutions:



The author regards these results as lending further support to the structural formula $\text{Pb} \begin{smallmatrix} \text{O} \\ \diagup \diagdown \\ \text{O} \end{smallmatrix}$ for lead peroxide. T. H. P.

Solutions of Metals in Non-metallic Solvents. III. Apparent Molecular Weight of Sodium Dissolved in Liquid Ammonia. CHARLES A. KRAUS (*J. Amer. Chem. Soc.*, 1908, 30, 1197—1219. Compare Abstr., 1907, ii, 935; this vol., ii, 486).—A study of the molecular weight of sodium and potassium in liquid ammonia was made by Joannis (Abstr., 1893, ii, 115; 1906, ii, 161) by determining the change in the vapour pressure of the solvent on addition of a known quantity of the metal. Franklin and Kraus (Abstr., 1899, ii, 202) determined the molecular weight of sodium and lithium in ammonia by the boiling-point method, and obtained results for sodium which were lower than those of Joannis. The results of Franklin and Kraus are regarded as the more trustworthy, as the solutions employed were less concentrated. The present investigation was undertaken with the object of determining the molecular weight of sodium in still more dilute solutions.

A method has been devised for measuring the changes of the vapour pressure of liquid ammonia on the addition of sodium, which gives results of an accuracy within about 1%, when the total pressure change is as small as 10 mm. The apparatus employed is described with the aid of a diagram. The determinations were made at about 15° , and the concentration varied from one to ten litres per gram-atom of sodium.

The results show that in dilute solutions the molecular weight of sodium is as low as 23, and in solutions of lower concentration than 0.1N is probably even lower. In the more concentrated solutions, the pressure change is smaller than would be expected from Raoult's law. The form of the complete vapour-pressure curve indicates that this deviation is due to a tendency of the solutions to separate into two phases, for which the critical point lies near 3 mols. % of sodium.

It has been shown previously (Abstr., 1907, ii, 936) that separation takes place in this region at lower temperatures. Raoult's law cannot therefore be applied to solutions of greater concentration than 0.1*N*.

E. G.

Solutions of Metals in Non-metallic Solvents. IV. Material Effects accompanying the Passage of an Electric Current through Solutions of Metals in Liquid Ammonia. Migration Experiments. CHARLES A. KRAUS (*J. Amer. Chem. Soc.*, 1908, 30, 1323—1344. Compare Abstr., 1907, ii, 935; this vol., ii, 486, and preceding abstract).—In the first paper of this series, it was suggested that the electrical conductivity of metals is due to ionisation. In this connexion, a study has now been made of the question as to whether the transport of matter accompanies the current through solutions of metals in liquid ammonia, and quantitative migration experiments have been carried out with solutions of sodium. Such solutions are well adapted for the purpose, since they possess a characteristic blue colour, which renders concentration changes visible in solutions as dilute as $N/40,000$. It has been found that the liquid at the surface of the anode becomes colourless, whilst at the cathode the colour becomes more intense. Experiments have also been made with solutions of potassium in potassamide dissolved in liquid ammonia. In this case, it has been found that the blue colour travels towards the anode, whence it might be concluded that the metal in the solution travels in this direction. It has already been shown, however, that the metal travels in the direction of the positive current, and the direction of movement of the colour is not therefore due to a movement of the metal in this direction, but is due to interaction between the negative metal anions and potassamide, whereby free metal is reversibly produced.

From the results of these experiments, it is concluded that the process of conduction in solutions of metals is ionic. The metal constitutes the positive ion, and is identical with the positive ion of a salt of the metal dissolved in ammonia. The negative ion consists of an electron surrounded by molecules of the solvent, and is in equilibrium with ammonia according to the equation: $e^-(\text{NH}_3)_n = e^- + n\text{NH}_3$. This electron is also in equilibrium with the metal cation and the neutral metal atoms, thus: $M^+ + e^- = M$, where M^+ is the cation and M the neutral atom.

E. G.

Oxidation of the Ammonia in Ammonium Persulphate. MARIO G. LEVI and E. MIGLIORINI (*Gazzetta*, 1908, 38, ii, 10—20. Compare Abstr., 1907, ii, 81).—Experiments made by heating solutions of ammonium persulphate at 100°, 75°, and 50° show that the ammonia of ammonium persulphate may undergo marked oxidation even in solutions which are originally neutral or almost so, and become more and more acid owing to the sulphuric acid liberated; this oxidation is rendered evident by the evolution of nitric oxide. The addition of sodium hydroxide in increasing proportions to the persulphate solution causes

the oxidation first to diminish to a minimum and then to increase indefinitely.

When no alkali is present, there seems to be a true oxidation of the ammonium ions, resulting in the formation of nitric acid in the solution. Corresponding with this oxidation, the amount of oxygen evolved is less than the theoretical quantity. When the decomposition takes place in presence of alkali, the reactions become more complicated; there may then be oxidation in the liquid phase and also in the gaseous phase, especially at the surface of the separation of liquid and gas, where the ammonia may be oxidised directly by part of the oxygen evolved. The courses of these two reactions would depend on the concentrations of the ammonia in the two phases; in general, oxidation takes place more readily and more rapidly in the liquid phase.

The oxidation is diminished in absolute amount by lowering the temperature, and is augmented by increasing the concentration of the persulphate.

T. H. P.

Combination of Nitrogen with Calcium Carbide. GINO POLLACCI (*Zeitsch. Elektrochem.*, 1908, 14, 565—566).—Potassium carbonate accelerates the combination of nitrogen and calcium carbide; the rate of combination is greatest when the mixture contains 4% of potassium carbonate. Increase of pressure also accelerates the reaction, but the acceleration practically reaches a limit at 2 atmospheres, further increase of pressure having little effect. Under the most favourable conditions, the conversion is complete in one hour at 900°.

T. E.

Preparation of Nitrides from Metallic Oxides or Salts with the Aid of Atmospheric Nitrogen. WILHELM BORCHERS and ERICH BECK (D.R.P. 196323). A metal capable of combining with nitrogen is used in the form of a fusible salt or of its oxide mixed with a fusible fluoride. The anode compartment resembles a gas-holder dipping into a layer of some fusible metal capable of forming a fusible alloy with the metal of the salt or oxide. The fused metallic salt or mixture of oxide and fluoride is placed within the inverted anode compartment and above the layer of fused metal. The anodes are composed of some refractory material, whilst the layer of fused metal forms the cathode. On electrolysis, the metal capable of combining with nitrogen is set free at the fusible cathode and alloys with it, and thus passes from under the anode compartment.

Arrived at the outer parts of the cathode vessel, the alloy meets a current of nitrogen, with which the liberated metal combines, forming a nitride which can be removed when necessary.

In preparing magnesium nitride, the cathode vessel contains fused zinc, and the anode liquid consists of a mixture of magnesia and an alkali fluoride.

On passing the current, the liberated magnesium alloys with the zinc, and subsequently combines with the nitrogen blown into the fused metal.

G. T. M.

Preparation of Alloys of Metals which Form Nitrides.

ERICH BECK (*Metallurgie*, 1908, 5, 504—521).—The conditions have been studied for the electrolytic preparation of alloys, especially of magnesium, capable of yielding ammonia on treatment with nitrogen and subsequent decomposition of the nitride by steam. Tin or lead may be used as the cathode metal. When the eutectic mixture of sodium and potassium fluorides (m. p. 702°) is used as the flux, magnesium oxide is readily dissolved, an addition of 10% lowering the m. p. to 677°, but, on electrolysis, only alkali metals are set free. A mixture of calcium and magnesium fluorides also dissolves magnesium oxide, and gives good results when the cathode metal is agitated. The eutectic point of calcium and magnesium fluoride lies at 945° and 48% CaF_2 ; mixed crystals are not formed. Barium and strontium fluorides, on the other hand, form only mixed crystals. Mixtures of barium fluoride with the calcium-magnesium fluoride eutectic give a curve having a marked eutectic point at 790°. By the addition of magnesium oxide to this mixture, the melting point is first depressed slightly, further additions raising it considerably. This mixture gives the best results, the magnesium oxide being added gradually, but owing to its high density, a part of the magnesium rises to the surface and is burnt.

If chlorides are used instead of the fluoride-oxide mixture, carnallite gives the best results. C. H. D.

Acid Phosphates. NICOLA PARRAVANO and ALDO MIELI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 33—41).—The authors have prepared the three acid phosphates: $\text{NaH}_2\text{PO}_4 \cdot \text{H}_3\text{PO}_4$; $\text{KH}_2\text{PO}_4 \cdot \text{H}_3\text{PO}_4$ (compare Staudenmaier, *Abstr.*, 1891, ii, 137), and $(\text{NH}_4)_2\text{H}_2\text{P}_2\text{O}_7 \cdot \text{H}_3\text{PO}_4$, of which they have determined the solubility in phosphoric acid and the behaviour towards water. The phosphoric acid used, m. p. 40.6°, was specially purified and freed from pyrophosphoric acid.

The sodium salt, $\text{NaH}_2\text{PO}_4 \cdot \text{H}_3\text{PO}_4$, forms rosettes of long needles or small prisms, m. p. 126—127°. The freezing-point curve of its aqueous solution has three branches, corresponding with the separation of ice, NaH_2PO_4 , and $\text{NaH}_2\text{PO}_4 \cdot \text{H}_3\text{PO}_4$ respectively.

The potassium salt, $\text{KH}_2\text{PO}_4 \cdot \text{H}_3\text{PO}_4$, for which Staudenmaier (*loc. cit.*) gave m. p. 127°, melts only partly at 127.5°, forming a liquid solution of KH_2PO_4 in H_3PO_4 , whilst part of the KH_2PO_4 remains in the solid state: $x(\text{KH}_2\text{PO}_4 \cdot \text{H}_3\text{PO}_4) \rightarrow [x\text{H}_3\text{PO}_4 + y\text{KH}_2\text{PO}_4] + [c - y]\text{KH}_2\text{PO}_4$; at 139° the whole of the KH_2PO_4 dissolves. The freezing-point curve of its aqueous solutions has two branches, corresponding with the separation of ice and KH_2PO_4 respectively.

The ammonium salt, $(\text{NH}_4)_2\text{H}_2\text{P}_2\text{O}_7 \cdot \text{H}_3\text{PO}_4$, forms shining, deliquescent needles, and, on heating, behaves like the potassium salt; at 77—78° it undergoes partial fusion, forming a solution of $(\text{NH}_4)_2\text{H}_2\text{P}_2\text{O}_7$ in H_3PO_4 , together with solid $(\text{NH}_4)_2\text{H}_2\text{P}_2\text{O}_7$, whilst at 118° perfect solution occurs. Its curve of solubility in phosphoric acid has two branches meeting at 78°, which is the transformation point of the salt; one branch corresponds with the separation of $(\text{NH}_4)_2\text{H}_2\text{P}_2\text{O}_7 \cdot \text{H}_3\text{PO}_4$, and

the other with that of $(\text{NH}_4)\text{H}_2\text{PO}_4$. In contact with water it decomposes rapidly. T. H. P.

Polyphosphates. NICOLA PARRAVANO and G. CALCAGNI (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 731—738).—The various supposed polyphosphates can be considered theoretically as formed by the union of pyrophosphate and metaphosphate in various proportions; thus the salt $\text{Na}_5\text{P}_3\text{O}_{10}$ is $\text{Na}_4\text{P}_2\text{O}_7 + \text{NaPO}_3$, the salt $\text{Na}_6\text{P}_4\text{O}_{13}$ is $\text{Na}_4\text{P}_2\text{O}_7 + 2\text{NaPO}_3$, and so on. The authors have accordingly studied the freezing-point curve of mixtures of sodium pyrophosphate and metaphosphate in various proportions as well as the curve obtained with the corresponding potassium salts. Both curves consist of two continuous branches meeting at a eutectic point; the shape of the curves indicates the non-existence of any compounds of metaphosphate and pyrophosphate, so that the various polyphosphates which have been described are probably mere mixtures of the two salts. W. A. D.

Action of Phosphoric Acid on Silicic Acid and Silicate Glass. KARL HÜTTNER (*Zeitsch. anorg. Chem.*, 1908, 59, 216—224. Compare Mylius and Meusser, Abstr., 1905, ii, 316).—When finely-powdered silica is heated in a quartz vessel with excess of metaphosphoric acid, a clear solution is at first obtained, from which, on continued heating, silicyl phosphate, $\text{SiO}_2\text{P}_2\text{O}_5$, separates in minute crystals (Hautefeuille and Margottet, Abstr., 1883, 782). The same compound is obtained by heating silicon chloride with phosphoric acid.

Silicyl phosphate is not decomposed by boiling water, but on heating strongly, it loses part of the phosphoric oxide and forms amorphous products, which are decomposed by water. The compound itself has also been obtained in an amorphous hydrated form from its solution in metaphosphoric acid, and this modification is being further investigated.

The action of phosphoric acid on the silicates found in glass has been investigated; in most cases, silicyl phosphate and metaphosphates are produced. Orthophosphoric acid scarcely acts on glass at the ordinary temperature, but does so at 100—150°. Phosphoric oxide can be sublimed in glass vessels without affecting them. G. S.

Silicic Acids obtained by Tschermak. JAKOB M. VAN BEMMELEN (*Zeitsch. anorg. Chem.*, 1908, 59, 225—247; *Chem. Weekblad*, 1908, 5, 567—589).—A criticism of the formula assigned to the silicic acids obtained by Tschermak (Abstr., 1905, ii, 815) by digesting natural silicates with hydrochloric acid. These formulae are based on the changes which are observed in the rate of loss of water by the hydrogels when the proportion of water to silica has attained certain values. According to the author, these changes cannot be supposed to differentiate between the chemically-combined and the mechanically-held water, and furnish no basis for the deduction of formulae for the various preparations of silicic acid. The hydrogels obtained from the silicates are colloidal absorption

compounds of indefinite composition, and the changes in the rate of dehydration are probably due to changes in the mechanical structure of the hydrogels brought about by the gradual removal of water.

H. M. D.

* **Dissociation of Molten Silicates. II.** CORNELIO DOELTEN. (*Monatsh.*, 1908, 29, 607—644. Compare this vol., ii, 178).—The paper deals with the conductivity and the polarisation of augite, albite, labradorite, and diopside in the molten and in the solid states at high temperatures. In measuring the conductivity of molten salts, a sharper minimum in the telephone is obtained by using electrodes set far apart and placed in a liquid of small cross section. Since the use of capillary vessels is excluded on account of the viscosity of molten silicates, the author employs a conductivity trough of quartz and kaolin of parallelepiped shape, 24—25 mm. long and 1 sq. cm. in area, in which the electrodes are fixed as in his former experiments, not quite at the ends of the vessel. The trough is filled with the powdered silicate, and the conductivity measured at temperatures up to those at which the silicate sinters and fuses. Both direct and alternating currents have been employed, but measurements by the former are only of secondary importance, and do not agree with the values obtained with an alternating current, except in the case of augite.

Experiments, mainly of a qualitative nature to ascertain whether polarisation occurs in the solid as well as in the liquid state, indicate that such a phenomenon is not manifest in crystalline silicates unless the vitreous modification is also present; only in the neighbourhood of the m. p. does slight polarisation occur. For example, with augite, m. p. about 1260°, polarisation is not evident below 1180°, but becomes quite distinct at 1250°; albite, which is especially liable to resolidify in the vitreous state, shows polarisation at 900°, and with strong currents at 1100°, electrolysis occurs, aluminium being deposited on the platinum cathode.

From van't Hoff's equation: $\log_e RT = -\frac{q}{RT^2}$ is derived the expression: $\log W = r/T + C$, according to which the graphic representation of the relation between the logarithm of the specific resistance, $W (=1/\kappa)$, and the reciprocal of the absolute temp., $1/T$ (r and C being constants), is a straight line. The author's experiments show that the formula only holds for temperatures removed from the m. p.

The conductivity of a crystalline silicate first becomes measurable at about 500°, increases with the temperature, and shows a marked augmentation in the neighbourhood of the m. p., causing the conductivity-temperature curve to show a break; a gradual rounding of the curve is exhibited when the molten silicate passes into the vitreous form. In general, the temperature-conductivity curve consists of two parts, one, corresponding with temperatures from 200° below the m. p. up to the m. p., is nearly vertical, and the other, representing the conductivity of the liquid phase, is nearly horizontal. The fact that a crystalline silicate shows a sudden change in conductivity when passing into the liquid or into the amorphous state, is the most important result of the investigation. The paper concludes with theoretical discussions

of the preceding fact and of the relation between crystalline structure and dissociation. C. S.

Search for Possible New Members of the Inactive Series of Gases. SIR WILLIAM RAMSAY (*Proc. Roy. Soc.*, 1908, 81, A, 178—180. Compare following abstract).—As the periodic system would appear to indicate the existence of two or three elements of the helium group heavier than xenon, the heavier portions of the gas, after the fractional distillation of 120 tons of liquid air, were investigated by Moore (*loc. cit.*); no positive result was obtained, and it is probable that higher members either do not exist in the atmosphere or that they disintegrate during the process of separation.

It is suggested that the emanations from radium, thorium, and actinium may be the missing inactive elements. Some support is lent to this view by the fact that the atomic weight of radium emanation (deduced from diffusion experiments) appears to be about 172, so that it would fit into the vacant space below neon. The most recent experiments, however, indicate that the atomic weight of the emanation may be over 200, which would bring it into the same horizontal period as radium, thorium, and uranium. Nothing very definite is known as to the respective atomic weights of the thorium and actinium emanations. G. S.

Heavy Constituents of the Atmosphere. RICHARD B. MOORE (*Proc. Roy. Soc.*, 1908, 81, A, 195—209).—The heavy gases from about 120 tons of liquid air have been examined for the presence of gases heavier than xenon, with negative results.

In the first experiment, the heavy residues from 19 tons of liquid air were condensed in liquid oxygen. After most of the oxygen had evaporated, the remainder was removed by means of melted phosphorus, and the nitrogen and other impurities were also removed by means of the appropriate reagents. The residue (about 6 litres of inactive gas) was then fractionated, but the final fraction was not heavier than xenon, and the spectrum afforded no evidence of the presence of a new gas. The water with which the gas had been in contact was boiled, and the gas given off added to the main bulk before fractionation.

In a second experiment, the residues from 100 tons of liquid air were worked up by a modified method, in which the gases did not come into contact with much water, but the results were negative in this case also. The methods of fractionation employed are fully described.

The magnesium and lime used to extract the nitrogen were examined to detect possible reaction products, with negative results. G. S.

New Reaction for the Production of Sodium Carbonate. Dr. CRISTO (*Bull. Soc. chim. Belg.*, 1908, 22, 292—295). The author finds that, contrary to previous statements, sodium carbonate can be rapidly and easily prepared by the interaction, under suitable conditions, of calcium carbonate and sodium silicate. A syrup of

sodium metasilicate is heated with chalk, the mass is then dried at a moderate temperature, and lixiviated with water to remove the sodium carbonate. The polysilicate, $3\text{SiO}_2\cdot\text{Na}_2\text{O}$, does not react with calcium carbonate.

Details are given of an industrial process for preparing the metasilicate from sodium sulphate by heating this salt with charcoal and sand.

W. O. W. . .

The Reciprocal Salt Pair $\text{NaCl-K}_2\text{SO}_4$; $\text{KCl-Na}_2\text{SO}_4$. ENNST JÄNECKE (*Zeitsch. physikal. Chem.*, 1908, 64, 343—356. Compare this vol., ii, 808).—The freezing-point and transformation curves of the four binary systems concerned confirm earlier results ($\text{KCl-K}_2\text{SO}_4$ and $\text{NaCl-Na}_2\text{SO}_4$, Ruff and Plato, Abstr., 1903, ii, 588; NaCl-KCl , Kunakoff and Schemtschuschny, Abstr., 1906, ii, 443; $\text{K}_2\text{SO}_4\text{-Na}_2\text{SO}_4$, Nacken, Abstr., 1907, ii, 611). The formation of a compound of sodium and potassium sulphates in the solid state, assumed by Nacken, is not confirmed.

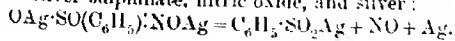
The results are recorded in a space model, the base of which is a square representing the proportions of the four salts present, and the ordinates are the temperatures of solidification. Two classes of mixed crystals are formed, and a minimum freezing point is found at the composition $(\text{Na}_2)_{43}(\text{K}_2)_{57}(\text{Cl}_2)_{50}(\text{SO}_4)_{24}$.

C. H. D.

The Silver Hydrogel in Photographic Films. LUPPO-CRAMER (*Zeitsch. Chem. Ind. Kolloide*, 1908, 3, 33—36).—Silver nitrate is reduced by pyrogallol and sodium carbonate to a black, finely-divided silver, which is quickly bleached by mercuric chloride, whereas pyrogallol alone gives a light-coloured, coarse-grained precipitate, to which mercuric chloride gives a dark colour. The author has tried many other reducing agents. In general, reduction in presence of a solvent of the silver salts, such as sodium sulphite, thiosulphate, or thiocyanate, or ammonia, tends to give the light-coloured silver, whilst any circumstance which tends to prevent the coalescence of the reduced silver, for example, reduction of an insoluble silver salt or enclosure of the salt in a gelatin film, yields the dark-coloured modification. The silver hydrogel of the photographic film is the dark-coloured form. Collodion does not hinder the coalescence of the silver particles to nearly the same extent as gelatin.

T. E.

Decomposition of Certain Salts of Silver. ANGELO ANGELI and GUERRIERO MARCHETTI (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 695—697).—Whereas the sodium salt of nitrohydroxylamic acid decomposes into sodium nitrite and hyponitrite, thus: $2\text{NaON}\cdot\text{NO}_2\text{Na} = \text{NaO}\cdot\text{N}\cdot\text{N}\cdot\text{ONa} + 2\text{NaNO}_2$, the silver salt gives silver nitrite, nitric oxide, and silver according to the equation: $\text{AgON}\cdot\text{NO}_2\text{Ag} = \text{NO}_2\text{Ag} + \text{NO} + \text{Ag}$. It is possible that the group NOAg is first eliminated and then decomposed; this view is strengthened by the fact that benzene-sulphydroxamic acid, which is decomposed by alkalis into benzene-sulphonic acid and a hyponitrite, gives an unstable silver salt, which readily forms silver sulphinate, nitric oxide, and silver:



Pernitrosocamphor gives a yellow silver derivative, which soon blackens, owing to the formation of silver and a substance, $C_{16}H_{15}O_2N_2$, which melts at 168° ; the change occurring is: $2C_{10}H_{15}O_2N_2 \cdot Ag = 2C_{10}H_{15}O_2N_2 + Ag_2$.
W. A. D.

Crystallisation of the Alkaline-earth Oxides, especially of Calcium Oxide, from their Nitrates. GOTTFRIED BRÜGELMANN (*Zeitsch. anorg. Chem.*, 1908, 59, 248—270).—When the carefully purified nitrates of calcium, strontium, and barium are heated to the temperature of decomposition, the corresponding oxides separate out in the form of regular cubes. Calcium and strontium oxides yield well-developed macroscopic crystals. The formation of the calcium oxide crystals is greatly facilitated by the addition of 0.25% to 0.6% of calcium hydroxide to the molten nitrate.

The author's very numerous experiments lead to the conclusion that the usual precautions adopted for the production of well-developed crystals (the use of large quantities of material, slow cooling, and freedom from mechanical disturbance) are not the only important factors of importance. A study of the crystallo-genetic peculiarities is essential.
H. M. D.

Relation of Changes of Solubility of Calcium Sulphate and its Rate of Hydration. PAUL ROHLAND (*Zeitsch. Elektrochem.*, 1908, 14, 421—422).—The effect of twenty-two substances on the rate of hydration of gypsum is tried. Those which increase the solubility of the gypsum in water, also increase its rate of hydration, and vice versa. The same substance may have opposite effects, for example, gypsum is less soluble in dilute solutions of sodium, ammonium, and magnesium sulphates than it is in water, whereas it is more soluble in strong solutions. Hydration is retarded by dilute solutions, and accelerated by strong ones.
T. E.

Preparation of Colloidal Amorphous Forms of Crystalline and Soluble Salts of the Alkaline earth Metals. P. P. VON WEIMARN (*Zeitsch. Chem. Ind. Kolloide*, 1908, 3, 89—91).—Gelatinous precipitates are obtained in general by rapid separation of a substance from a solution in which it is very sparingly soluble. High viscosity of the solvent is also favourable. The thiocyanate of an alkali or alkaline-earth metal is dissolved in a mixture of amyl alcohol and ether, and mixed with a similar solution of an acid. In this way the following salts have been obtained in the gelatinous form: potassium, sodium, ammonium, calcium, strontium, and barium chlorides, bromides, and nitrates, and the sulphates of potassium, sodium, and ammonium. The sulphates and phosphates of the alkaline-earth metals are obtained in the gelatinous form from solutions in any of the lower aliphatic alcohols.
T. E.

Isomorphism of Calcium and Manganese Bisilicates. A. S. GINSBERG (*Zeitsch. anorg. Chem.*, 1908, 59, 346—363).—A freezing-point curve for the system wollastonite-rhodonite has been obtained by observations on mixtures containing different proportions

of the two silicates. Calcium silicate melts at 1512° ; manganese silicate at 1218° . The temperatures corresponding with the commencement of crystallisation and with complete solidification are given for a series of mixtures. The minimum temperature of 1180° corresponds with a mixture containing 12.8 molecular % of calcium silicate.

From the nature of the freezing point diagram, the conclusion is drawn that the two silicates form a complete series of mixed crystals, and that wollastonite and rodonite are isomorphous. Since rhodonite is triclinic, the existence of a polymorphic, monoclinic modification must be assumed in order to explain the formation of the monoclinic series of mixed crystals, with which the mineral bustamite is to be identified.

Measurements of the density and hardness of mixtures containing various proportions of the two silicates have been made, which show that these properties vary continuously with the composition. The curve representing the hardness as a function of the composition exhibits a maximum for a mixture containing 15% manganese silicate. The density of wollastonite is 2.919, and that of rhodonite 3.350.

H. M. D.

Action of Soluble on Insoluble Substances. WILLIAM OECHSNER DE CONINCK and L. ARZALIER (*Bull. Acad. roy. Belg.*, 1908, 577—578. Compare *Abstr.*, 1907, ii, 952).—When barium sulphate (1 mol.) is heated at 100° for 620 hours with methylamine hydrochloride (2 mols.) in aqueous solution, a partial double decomposition ensues. A similar result was also obtained in the case of barium sulphate (1 mol.) and an aqueous solution of potassium chloride (2 mols.) at the end of five months, heated at $90-95^{\circ}$ during two-fifths of the period.

M. A. W.

Action of Soluble on Insoluble Substances. WILLIAM OECHSNER DE CONINCK and L. ARZALIER (*Bull. Acad. roy. Belg.*, 1908, 607—608).—Pure strontium carbonate, shaken with a concentrated solution of potassium chloride gives, in four months, a solution containing strontium chloride.

E. H.

Microscopic Study of Mortar. GINO GALLO (*Gazzetta*, 1908, 38, ii, 142—156. Compare *Stern*, this vol., ii, 589).—Microscopic study of the changes occurring in a mortar shows that the absorption of carbon dioxide by the calcium hydroxide present is intimately related to the presence of water, and, since the calcium carbonate formed is distinctly crystalline, it is concluded that both the lime and the carbon dioxide must be in solution before the reaction takes place. A mortar prepared with a deficit of water lacks solidity and has low resisting properties, owing to the fact that the calcium carbonate formed under these conditions forms a coarse net-work; similar defects are observable in mortar made with coarse sand, the calcium carbonate deposited in the large interstices not adhering to all the neighbouring sand granules.

The injurious effect exercised by the presence of magnesia in a mortar is explained by the slight solubility of the magnesia in the

water present and by the slow absorption of carbon dioxide by the solution formed.

When the water is completely eliminated from a mortar, chemical action ceases, and in the interior of old mortars in which the carbon dioxide could not reach the lime before the water evaporated completely, free lime is found.

T. H. P.

Microscopic Study of Mortar and Pozzuolana. GINO GALLO (*Gazzetta*, 1908, 38, ii, 156—204).—The author reviews briefly previous work on pozzuolana and its value as a hydraulic mortar. His own experiments on the setting of mortars prepared from pozzuolana were made with the microscope (see preceding abstract).

All the mortars examined exhibited a distinctly crystalline border of calcite, which forms immediately the mortar is made, and has a thickness of about 0.1 mm.; when good pozzuolana is employed, the thickness of this layer does not change appreciably. This calcitic coating prevents water from finding ready access to the interior of the mortar, and so hinders the solution and removal of the lime.

The first phenomenon observable in the setting of these mortars is the hydration, by means of the lime water, of the silica and alumina, which swell so as to fill the whole space previously occupied by air and water, and yield an impermeable mass bestowing resistance on the mortar. Then follows the formation of soluble calcium aluminate, which, in presence of excess of lime and in supersaturated solution, deposits crystals of the calcium aluminate, $\text{Al}_2\text{O}_3 \cdot 3\text{CaO} \cdot 10\text{H}_2\text{O}$, which is stable only in presence of calcium hydroxide solution, and is decomposed by water; this crystallisation binds together the various particles which exist as inclusions in the crystals. The limiting surfaces between the flocculent portions and the spaces left by these then become the seat of capillary forces, by means of which the silica attracts the lime into its pores and thus forms nodules in which the lime gradually gives up its water of hydration and crystallises as calcium monohydrate, thus determining complete adhesion of the various parts. The more rapidly the swelling attains its maximum and the greater the latter, the more satisfactory will be the setting of the mortar.

The increases in volume of various specimens of pozzuolana in presence of calcium hydroxide solution have been measured. It is found that this increase is related directly to the amount of lime absorbed, and that it is considerably increased by renewing the calcium hydroxide solution from time to time. The action of calcium hydroxide also causes an increase in the amounts of alumina and silica which can be dissolved by dilute acid.

The value of a pozzuolana for the preparation of hydraulic mortar may be determined by the following measurements: (1) Increase of volume with calcium hydroxide solution. (2) Electrical conductivity (compare Georgis and Gallo, *Abstr.*, 1906, ii, 447). (3) Amounts of silica and alumina dissolved by treating with 5% sodium hydroxide solution on the water-bath for fifteen minutes. For good pozzuolana, these amounts are almost constant, even where the material has

been previously treated with dilute acid; but for inferior materials, such as ashes from Vesuvius and Bassano, previous disgregation with hydrochloric acid renders increasing amounts of silica and alumina capable of solution in 5% sodium hydroxide solution. T. H. P.

Liquefaction and Sublimation of Certain Sulphides. WILHELM BILTZ (*Zeitsch. anorg. Chem.*, 1908, 59, 273—284).—The sulphides, contained in porcelain or magnesia tubes through which a current of dry nitrogen was passed, were heated by means of an electrical resistance furnace. The sublimation or liquefaction was observed by means of a telescope, the temperature being registered by a thermo-element or a Wanner pyrometer. The following melting points are recorded: synthetic lead sulphide, 1100° , sublimation commencing at 950° ; galena from Freiberg, $1112^\circ \pm 2^\circ$; ferrous sulphide, $1197^\circ \pm 2^\circ$; nickel sulphide, $797^\circ \pm 2^\circ$; cobalt sulphide, $>1100^\circ$. Zinc, cadmium, and mercuric sulphides sublime without melting. The temperatures at which sublimation begins are as follows: zinc blende from Santander, $1178 \pm 2^\circ$; synthetic zinc sulphide in the form of wurtzite, $1185^\circ \pm 6^\circ$; cadmium sulphide, 980° ; cinnabar and precipitated mercuric sulphide, $446^\circ \pm 10^\circ$.

Stannous sulphide exhibits two melting points. Its behaviour was traced by a study of cooling and heating curves. The lower melting point is about 870° , and, as the temperature is raised from 1000° to 1100° , the viscosity of the liquid increases very quickly, so that at the latter temperature the substance exhibits the properties of a solid. At about 1200° , liquefaction again takes place. The phenomenon has not yet been explained. H. M. D.

Compounds of Lead with Nitrous Acid. ALBERTO CHILESOTTI (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 824—834).—The author gives a résumé of the various lead nitrites which have been described, many of which are probably not individual compounds.

By mixing equivalent proportions of solutions of lead chloride and silver nitrite saturated at 25° and concentrating the liquid, first by freezing and then by evaporation over sulphuric acid, he has obtained the hydrate, $\text{Pb}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$ (compare Lang, *J. pr. Chem.*, 1862, 86, 300), and the anhydrous salt, $\text{Pb}(\text{NO}_2)_2$, mixed with a little lead oxide and lead nitrate. The electrical conductivity of lead nitrite solutions at 25° is as follows:

$\kappa = 16$	32	64	128	256	512	1024
$\Lambda = 59.1$	72.3	65.5	98.9	111.3	122.1	129.7

For the more concentrated solutions, the conductivity of the nitrite is somewhat less than that of the nitrate or chloride, but at greater dilutions the differences are small. The value of $\Lambda_{\infty} - \Lambda$ is 27.6 for the nitrate, 42.1 for the chloride, and 57.1 for the nitrite. It is probable, from their conductivity and from their intense yellow colour, that solutions of lead nitrite contain complex anions of the type $\text{Ag}(\text{NO}_2)_2^-$ or $\text{Hg}(\text{NO}_2)_2^-$ (compare Abegg and Pick, *Abstr.*, 1906, ii, 833). T. H. P.

Planimetric Analysis of Alloys and the Structure of Phosphor Copper. ALFRED K. HUNTINGTON and CECIL H. DESCH (*Trans. Faraday Soc.*, 1908, 4, 51—58).—The method depends on the measurement, by means of a planimeter, of the relative areas, occupied by the different constituents on a polished and etched section of an alloy. It is applicable to alloys for which two solid constituents are visible in the same section, and often also when crystals of a solid constituent are surrounded by a eutectic, but is only to be employed when the alloys are in a known state of equilibrium.

In making an observation, the highly magnified image of the section is projected on a sheet of paper, the outlines of one of the constituents traced with a pencil, and the crystals shaded. A boundary line is drawn to enclose the pattern to be measured, and the shaded area measured with the planimeter. The agreement of planimetric and ordinary analysis for the alloys of copper and aluminium is excellent. The chief recommendation of the method is its rapidity.

When the pattern is very complicated, or made up of many small and detached portions, better results are obtained by dividing the field into squares, estimating the relative shaded areas, and averaging.

Heyn and Bauer, who have investigated the phosphor-copper alloys (Abstr., 1906, ii, 855), observed that the copper areas determined planimetrically were larger than calculation from the composition would indicate. The alloys in question (up to 8% phosphorus) consist mainly of copper crystals and a eutectic copper—copper phosphide, and it is now shown that the difference is due to the fact that the crystals of copper gradually increase in size after solidification by withdrawing copper from the eutectic surrounding them, so that each crystal is surrounded by a clear belt free from copper. The areas of these belts have been determined, and when a corresponding correction is applied to the areas of the copper crystals, the results of the planimetric and direct analysis show excellent agreement.

The paper is illustrated with photomicrographs.

G. S.

Constitution of the Copper-Zinc-Nickel Alloys, and of the Binary Systems Copper-Nickel, Copper-Zinc, and Nickel-Zinc. VIKTOR E. TAFEL (*Metallurgie*, 1908, 5, 343—352, 375—383, 413—430).—The study of the copper-nickel equilibrium diagram completely confirms the results of Guertler and Tammann (Abstr., 1907, ii, 174). The results obtained for the copper-zinc series differ somewhat from those of Shepherd (Abstr., 1904, ii, 662). The existence of the compound Cu_2Zn_3 (m. p. 830°) is established, and that of the compound CuZn , indicated by other methods, is quite consistent with the thermal diagram. The compounds CuZn_2 , CuZn_3 , CuZn_4 , CuZn_5 , and CuZn_6 , described by various authors, certainly do not exist. The alloys, especially in the neighbourhood of 50% Zn, have considerable tendency to liquefy.

The nickel-zinc alloys (this vol., ii, 105; compare Voss, *ibid.*, ii, 197) have been more fully investigated. The only compound recognised is NiZn_3 , a highly brittle substance giving a characteristic coloration with dilute nitric acid. Owing to loss of zinc by volatilisation

tion, it was found necessary to complete the diagram above 50% Ni by extrapolation from the ternary model.

Alloys of copper, nickel, and zinc liquate considerably, the lower portions of the ingots becoming generally richer in nickel. The thermal diagram, constructed as a projection on a triangular base, represents determinations of 92 different alloys. Neither a ternary compound nor a ternary eutectic point was found. The surface of the temperature-concentration model consists of three surfaces, each representing the separation of a series of primary mixed crystals. The third of these, the richest in zinc, is separated from the second by a eutectic line. The observations have also been plotted in the form of vertical sections through the model, the complicated changes taking place in the solid alloys being also represented in this way.

The alloys of technical importance, such as German silver, consist of homogeneous mixed crystals. Alloys containing 15.3—20% Ni, 73—80% Cu, and 7% Zn have a remarkable resemblance to silver, both in their colour when polished and in ductility.

The structure of the alloys, and the transformations undergone during cooling, are illustrated by fifty photomicrographs.

C. H. D.

Cuprous Ammonia Halides. STEWART J. LLOYD (*J. Physical Chem.*, 1908, 12, 398—403).—Evidence of the existence of various cuprous ammonia halides was obtained by saturating the cuprous halides at 0° with dry ammonia, and measuring the vapour pressure at a constant temperature as the ammonia was gradually removed. The curves, obtained by plotting vapour pressures against the ammonia content of the halides, show discontinuities in the vapour pressure corresponding with the following compounds, of which the colour and the approximate melting point are recorded: $\text{Cu}_2\text{I}_2 \cdot 6\text{NH}_3$, light green, 105°; $\text{Cu}_2\text{I}_2 \cdot 3\text{NH}_3$, dark brown, 117°; $\text{Cu}_2\text{Br}_2 \cdot 6\text{NH}_3$, green, 115°; $\text{Cu}_2\text{Br}_2 \cdot 3\text{NH}_3$, brown, 135°; $\text{Cu}_2\text{Cl}_2 \cdot 6\text{NH}_3$, green, 123°; $\text{Cu}_2\text{Cl}_2 \cdot 3\text{NH}_3$, light brown, 144°; $\text{Cu}_2\text{Cl}_2 \cdot \text{NH}_3$, dark brown, 162°. Tables are given which show the vapour pressures of the seven compounds at a series of different temperatures.

H. M. D.

Dissociation Pressures of Certain Oxides of Copper, Cobalt, Nickel, and Antimony. HARRY W. FOOTE and E. K. SMITH (*J. Amer. Chem. Soc.*, 1908, 30, 1344—1350).—The dissociation pressures of cupric oxide, cuprous oxide, cobalto-cobaltic oxide, cobaltous oxide, nickelous oxide, and antimony tetroxide have been measured at temperatures between 800 and 1245°. When possible, the temperature has been determined at which the dissociation pressure equals the pressure of the oxygen in the air. Cupric oxide gives this pressure at about 1025°, cobalto-cobaltic oxide at about 905°, and antimony tetroxide at about 950°. The dissociation pressure of cuprous oxide does not exceed 1 mm. at 1020°. Pure cobaltous oxide does not show a dissociation pressure at 1100°.

The dissociation pressures of cupric oxide and nickelous oxide calculated by Stahl (*Metallurgie*, 1907, 4, 682) from Nernst's formula are much lower than those now obtained by direct measurement.

E. G.

Reduction of Fehling's Solution to Metallic Copper. Deposition of Copper Mirrors on Glass. PUNCHANAN NEOGI (*Zeitsch. anorg. Chem.*, 1908, 59, 213—215).—To obtain a mirror by reduction of Fehling's solution, the copper sulphate solution is poured into a beaker, the tartrate solution added until the precipitate at first formed just disappears, a considerable amount of formaldehyde is then added, the beaker inclined, and heated on one side until the deposition of copper just begins. On rotating the beaker, a mirror forms all over the inner surface. One of the precipitates thus produced contained 98.6% of copper. G. S.

Oxidation by means of Cuprous Oxide in Strongly Alkaline Solution. RICHARD EURENFELD (*Zeitsch. anorg. Chem.*, 1908, 59, 161—182).—An attempt was made to estimate cupric salts volumetrically by reducing them completely to the cuprous form by the action of an arsenite in strongly alkaline solution, the excess of arsenite being determined by titration with iodine, but the results came out about 6% too high. This result is due to the simultaneous oxidation of part of the arsenite by the oxygen of the air under the catalytic influence of cuprous oxide.

In the absence of a reducing agent, cuprous oxide in the presence of strong alkali undergoes autoxidation, and more than the theoretical amount of oxygen required for the formation of cupric oxide is absorbed. It is probable that the excess of oxygen goes to the formation of hydrogen peroxide, which is, however, immediately used up in oxidising more cuprous oxide. Autoxidation of cuprous oxide also takes place in the presence of concentrated sulphuric acid, excess of oxygen being absorbed and hydrogen peroxide formed.

Strongly alkaline solutions of antimony trichloride behave exactly like arsenite solutions, and the oxidation of alkaline sodium sulphite and stannous chloride solutions is also accelerated by cuprous oxide. In the latter case, however, only the theoretical volume of oxygen is absorbed. On the other hand, cuprous oxide does not accelerate the oxidation of chromic sulphate, potassium nitrite, potassium phosphite, or potassium hypophosphite in alkaline solution. Potassium phosphite and hypophosphite and sodium sulphite are more readily acted on by the oxygen of the air in aqueous than in strongly alkaline solution. G. S.

Solubility of Precipitated Basic Copper Carbonate in Solutions of Carbon Dioxide. E. E. FREE (*J. Amer. Chem. Soc.*, 1908, 30, 1366—1374).—In connexion with a study of the effect of mine effluents in irrigation waters, it was found necessary to ascertain the solubility of precipitated basic copper carbonate in water containing varying amounts of carbon dioxide, and the influence of certain salts on it. The precipitate obtained on mixing solutions of copper sulphate and sodium carbonate is at first pale bluish-green, but gradually loses carbon dioxide and becomes of a malachite-green colour. The latter product is regarded by Gröger (*Abstr.*, 1900, ii, 542) as the compound $6\text{CuO} \cdot 3\text{CO}_2 \cdot 4\text{H}_2\text{O}$. It has now been found that the substance is of variable composition, and is so changed by the

action of carbon dioxide and water that it gradually becomes less soluble in the carbon dioxide solution. On repeatedly treating such precipitates with solution of carbon dioxide of 0.12% strength, they finally reach a constant solubility of about thirty-five parts per million, but the solubility increases with the concentration of the carbon dioxide. The solubilities are but little changed by the addition of small quantities of sodium chloride or sulphate, but are increased by larger amounts of these salts. Sodium and calcium carbonates decrease the solubility greatly, but calcium sulphate does not cause a decided change in either direction.

E. G.

Resolution of Ytterbium into its Components. GEORGES URBAIN (*Chem. Zeit.*, 1908, 32, 730).—The author disputes Welsbach's claim for priority, and states that the decomposition products, neoytterbium and lutetium, which he obtained (*Abstr.*, 1907, ii, 956) are identical with those of Welsbach, called by him aldebaranium and cassiopeium (this vol., ii, 591).

J. V. E.

Interaction of Aluminium Powder and Carbon. FRANK E. WESTON and H. RUSSELL ELLIS (*Trans. Faraday Soc.*, 1908, 4, 60—71. Compare Fichter, *Abstr.*, 1907, ii, 691).—The interaction of finely-powdered aluminium and finely-powdered wood-charcoal, sugar-charcoal, and graphite has been investigated. In all cases, mixtures could be prepared which, when started with a fuse of magnesium and barium peroxide, reacted with vivid incandescence, like the ordinary thermit reaction. Some mixtures, when raised to a dull red heat in a closed crucible, reacted vigorously on exposure to the air.

In all cases the reaction product contained aluminium carbide, nitride, and oxide, as well as the free elements. As the only hydrocarbon obtained by the action of water or hydrochloric acid on the product is methane, it is probable that the only carbide formed is Al_4C_3 .

The authors consider that the air plays a prominent part in the phenomenon, that the first action is the oxidation of the carbon to monoxide and dioxide, the heat given out starts the oxidation of the aluminium, and, finally, the latter reaction raises the temperature sufficiently to bring about combination of the aluminium with carbon and nitrogen. Among other reasons in support of this view, it was found that, when the air was withdrawn from the mixtures by means of a Töpler pump, it was much less easy to initiate combination.

G. S.

Corrosion of Iron by Water and Water Solutions. E. HEYLAND and O. BAUER (*Chem. Zentr.*, 1908, i, 2063—2065; from *Mitt. K. Mont.-polyt. Amt, Gross-Lichterfelde*, 1907, 26, 1—104. Compare Friend, this vol., ii, 638).—A. *Influence of Oxygen and Carbon Dioxide on the Corrosion of Iron by Water and by Water Solutions.*—The rusting was estimated by allowing small, weighed wrought iron plates to rust when suspended in Charlottenburg conductivity water, or aqueous solutions contained

in a glass beaker, and re-weighing them after removing the rust. Air was allowed free access to the iron and water; in some cases, it was drawn through the liquid, and the temperature was that of the ordinary room. The results obtained support the conclusions of Traube (Abstr., 1885, 1105) and Dunstan (Trans., 1905, 87, 1548), that carbon dioxide is not needful, but the presence of free oxygen is a necessary condition for the process of rusting; also, that the iron does not derive oxygen from the water, but from the atmosphere. After discussing the conditions that influence the rate of rusting, the authors cite some experiments which show that the addition of hydrogen peroxide does not increase the rate of rusting so much as does drawing air through the liquid in which the iron is suspended.

B. Rusting Influenced by the Iron being in Contact with other Metals.—Copper when in contact with the iron is found to increase the rusting 25% when suspended in conductivity water and 47% in artificially-prepared sea-water. In contact with nickel, iron rusts 14—19% more than it does by itself, and ingot-iron in contact with cast-iron rusts less readily than when by itself, whilst the cast-iron rusts more readily by about 50%. It is found that iron in contact with a more positive metal, suspended in a liquid causing rusting, rusts less readily, and when in contact with a more negative metal, rusting takes place more readily than when iron is exposed under similar conditions by itself.

C. Comparison of the Rusting of Various Kinds of Iron by Water.—The results show that a content of 0.46 to 3.08% of manganese and 0.072 to 3.38% of phosphorus has very little influence on the rate of rusting.

D. Influence of Various Liquids on the Rusting of Iron at the Ordinary Temperature.—It is found that very dilute solutions of simple electrolytes generally cause iron to rust more slowly than does distilled water alone; with increase of concentration, however, the rusting increases, reaching a maximum and then decreasing slowly. The solutions showing maximum activity are called "critical solutions," and generally cause iron to rust more readily than distilled water. Exceptions to this, however, are solutions of potassium chloride, sodium chloride, potassium sulphate, sodium hydrogen carbonate, sodium sulphate, calcium chloride, and barium chloride, the activity of which is less than that of distilled water. Ammonium nitrate solution and a saturated solution of diammonium hydrogen phosphate cause iron to rust, probably owing to their decomposition, and thus appear to contradict the previous conclusion; the behaviour of the "critical solution" of diammonium hydrogen phosphate is also abnormal.

In the case of certain salt solutions when the concentration is increased beyond the "critical concentration," the rusting is very rapidly decreased, until a concentration is reached where no rusting takes place; such solutions are called "limiting solutions." Diammonium hydrogen phosphate again behaves in a distinctive manner, having a second limiting concentration, and, finally, in still more concentrated solutions, iron is dissolved with liberation of a gas.

E. Electrical Potential between Iron and Various Liquids.—This section not being suitable for abstraction, the original should be consulted.
J. V. E.

Alloys of Iron, Silicon, and Carbon. W. GONTERMANN (*Zeitsch. anorg. Chem.*, 1908, 69, 373—413).—The investigation covers that portion of the iron-carbon-silicon system which includes the components $\text{Fe-Fe}_3\text{C-FeSi}$. Pure iron-carbon alloys were fused with silicon in porcelain tubes in an atmosphere of purified nitrogen. Repeated melting was sometimes necessary to ensure homogeneity.

Iron containing only 0.7% carbon exhibits a transformation point at 1411° , which appears on both the heating and cooling curves, and does not disappear on re-heating, but is absent from alloys containing even a slightly larger proportion of carbon. Owing to undercooling, alloys containing 3—4% C may contain both structurally-free martensite and cementite. A hypothetical equilibrium curve is suggested for the iron-carbon alloys, assuming the existence of two immiscible liquid phases above 3—4% C, one of which readily sets free graphite. The behaviour of white and grey cast-irons may be explained on this assumption. The transformation observed at 800° may be the eutectoid point of β -iron and graphite. Slight modifications are also suggested in the iron-silicon diagram (compare Guertler and Tammann, *Abstr.*, 1906, ii, 32).

The ternary equilibrium is represented by projections on the base of the space-model. The freezing points lie on two surfaces, on one of which an Fe-C-Si solid solution separates (silicon-martensite), and on the other an $\text{Fe}_3\text{C-FeSi}$ solid solution (silicon-cementite), the two intersecting along a eutectic line. At lower temperatures, the stable system consists of silicon-ferrite and graphite, but the reaction is slow and the development of heat very small, so that the exact position of the curve of separation of graphite could not be determined. The only part of the metastable system which could be satisfactorily followed was the eutectoid line between silicon-ferrite and silicon-cementite (silicon-pearlite). Alloys consisting of unsaturated silicon-martensite undergo the metastable change on cooling under the conditions adopted, whilst saturated silicon-martensite, or a mixture of this with silicon-cementite, sets free graphite (stable change) if the silicon-content exceeds 1%. Silicon-cementite containing more than 20% Si does not undergo transformation in the solid state.

C. H. D.

The Thomas Steel Process. F. WUST and L. LAVAL (*Metallurgie*, 1908, 5, 431—462, 471—489).—The relative rate of oxidation of the various elements present in pig-iron during the Thomas basic steel process has been studied experimentally. From 8 to 10% of iron is lost during oxidation, mostly during the last stage of the process, when the last traces of phosphorus are being removed. This increases with rise of temperature, the tendency of iron to oxidise increasing more rapidly with temperature than that of phosphorus. The conditions are not altered by drying or heating the air supply. Curves are given showing the change in composition of metal and slag during the process.

The changes in structure of the alloys are illustrated by photomicrographs. The original phosphoretic iron contains crystals of cementite and martensite and a ternary cementite-martensite-phosphide

eutectic, as well as well-formed crystals of sulphide. With progressive elimination of carbon, the ternary eutectic is replaced by a binary martensite-phosphide eutectic.

C. H. D.

Dissociation Pressures of Ferric Oxide. PERCY T. WALDEN (*J. Amer. Chem. Soc.*, 1908, 30, 1350—1355).—Determinations of the dissociation pressures of ferric oxide have been made at temperatures between 1100° and 1400°. At 1350°, the pressure is approximately equal to that of the oxygen in the air. Ferrosoferric oxide does not show any dissociation pressure at 1350°.

By heating cuprous oxide with ferric oxide, Stahl (*Metallurgie*, 1907, 4, 688) obtained a strongly magnetic product, and concluded that the following reaction had occurred: $\text{Cu}_2\text{O} + 3\text{Fe}_2\text{O}_3 = 2\text{CuO} + 2\text{Fe}_3\text{O}_4$. It is now shown that this magnetic substance was probably the compound CuFe_2O_4 described by List (*Abstr.*, 1879, 13). It is probable that there is another magnetic double oxide of iron and copper which has not yet been described, and work on this and similar substances is in progress.

E. G.

Ferritinosulphides. LIVIO CAMBI (*Atti R. Accad. Lincei*, 1908, [v], 720—724).—A theoretical paper in which facts already abstracted (*Abstr.*, 1907, ii, 960; this vol., ii, 41, 288) are discussed at length with particular reference to the views of Bellucci and Cesaris (*Abstr.*, 1907, ii, 29, 472; this vol., ii, 111, 499, 593).

W. A. D.

Gases Occluded in a Special Nickel Steel. G. BELLOC (*Compt. rend.*, 1908, 147, 211—215. Compare this vol., ii, 198).—The proportion and nature of the gases occluded by a nickel steel containing about 43% of nickel and 0.15% of carbon have been determined by the method described previously. The occluded gases consist of carbon monoxide and dioxide, hydrogen, and nitrogen, the first being completely evolved below 520°, whilst the last only commences to be evolved above this temperature. Different results are obtained according as the steel is in the form of wire or shavings. In the latter case, the total gas evolved is 3.5 times the volume of the alloy; the curve obtained by plotting the variation of the volume of the gas evolved with the temperature (dv/dt) against the temperature (v) is sensibly parallel to the temperature axis, and the proportion of carbon monoxide increases up to 75%, whilst the maximum amount of hydrogen is evolved at 540°, above which the volume of hydrogen produced gradually decreases. With the wire the total volume of gas evolved is ten times that of the metal; the curve (in t , dv/dt) exhibits well-defined maxima at 540° and 830°, and the variations in composition of the gas are no longer gradual; thus at 540° a minimum proportion of carbon monoxide and a maximum of hydrogen are observed, whilst above this temperature the carbon monoxide increases somewhat irregularly. The mean proportion of hydrogen is greater than from the shavings.

This alloy belongs to the type termed by Guillaume "reversible," the limits of its gradual transformation being 350° and 400°. The greater part of the gases is evolved while the iron is in the γ -state; and

the nickel in the β -state, from which would be expected a gradual alteration in the composition and volume of the gas evolved. The latter is the case with shavings, and the different behaviour of the wire indicates an alteration in its molecular state. The difference in absolute volumes of the gas evolved from shavings and from wire can be explained either by (1) unequal distribution in the ingot, or (2) large mechanical loss of occluded gas in turning, or (3) absorption of gas during the manufacture of the wire. E. H.

Action of Arsenic Chloride and Arsenic on Cobalt. F. DUCELLIEZ (*Compt. rend.*, 1908, 147, 424—426).—By the action of arsenic chloride, metallic cobalt is transformed into a mixture of chloride and arsenide, the composition of the latter ranging from CoAs_2 to Co_3As_2 according as the temperature of the reaction is increased. When mixtures of arsenic chloride with cobalt or alloys of arsenic and cobalt, or mixtures of arsenic and cobalt (both components being powdered), are heated in an inert atmosphere (hydrogen or carbon monoxide), or when powdered cobalt is heated in a current of hydrogen containing arsenic vapour, the following results are obtained. Between 800° and 1400° , *tricobaltarsenide*, Co_3As_2 , is formed, and above 1000° is obtained as brilliant ingots, D° 7·82, which lose arsenic about 1400° . From 600° to 800° , cobalt or the arsenide, Co_3As_2 , is converted into *cobalt arsenide*, CoAs , a grey, crystalline powder, D° 7·62, which tarnishes slightly in the air, and when heated in a current of hydrogen commences to lose arsenic at 800° without melting. At 400 — 600° , the final product contains 65·6% of arsenic corresponding with the composition Co_3As_2 ; it has D° 7·35, and commences to decompose at 600° . Below 400° , the preceding compound is slowly transformed into smaltine, CoAs_2 , which is not directly obtained at these temperatures by the action of arsenic trichloride on cobalt. The product is a grey powder, D° 6·97, oxidised by the air, and decomposed slightly above 400° . In the experiments above 600° , a little arsenic is set free, the amount increasing with the temperature. In the first two series of experiments, after the arsenide is formed, continued action of arsenic chloride results in the formation of cobalt chloride and liberation of arsenic, the weight of the compound diminishing. In the last two cases, arsenic is not deposited or cobalt chloride formed after the production of Co_3As_2 or CoAs .

The compound Co_3As_2 can also be prepared by reducing cobalt arsenate or arsenite with hydrogen at 900° ; the heat developed, volatilising part of the arsenic, prevents the formation of cobalt arsenide, CoAs .

The arsenides described are non-magnetic, and their densities are much higher than those found by calculation for mixtures. They are violently attacked by chlorine, oxygen, and sulphur, readily dissolved by nitric acid and aqua regia, and slowly attacked by fused alkalis and alkali carbonates, but not concentrated hydrochloric acid has very little action, and sulphuric acid still less. E. H.

Alloys of Cobalt with Tin, Antimony, Lead, Bismuth, Thallium, Zinc, Chromium, and Silicon. KURT LEWONJA (*Zeitsch. anorg. Chem.*, 1908, 59, 293—345).—Freezing-point curves

of mixtures of the metals have been obtained and the micro-structure of the solidified products examined.

Cobalt and tin are miscible in all proportions in the liquid condition. The compounds Co_2Sn , m. p. 1151° , and CoSn , which melts with decomposition at 943° and undergoes a polymorphic change at 526° , are formed. In the solid condition, the maximum amount of tin dissolved by cobalt is 3.5%.

Cobalt and antimony are completely miscible in the liquid state. The compounds CoSb , m. p. 1191° , and CoSb_2 , which melts with decomposition at 879.5° , are formed. In the solid state, antimony is soluble to the extent of 12.5% in cobalt.

Cobalt and lead are partly miscible in the liquid state; molten alloys containing more than 3% or less than 99% of cobalt cannot be obtained. Neither compounds nor mixed crystals are formed in the solid state.

The behaviour of cobalt and bismuth is similar to that of cobalt and lead, the limits of miscibility in the liquid state being represented respectively by 6% and 93% of cobalt.

Cobalt and thallium are only slightly miscible both in the liquid and solid state, and there is no evidence of the formation of definite compounds.

Cobalt and zinc yield mixed crystals when the percentage of cobalt in the fused mass varies from 0.5 to 18.5. The saturated mixed crystals contain 13.4% cobalt. Evidence has also been obtained of the formation of a compound CoZn_4 .

Cobalt and chromium are miscible in all proportions both in the liquid and solid state. The minimum temperature at which crystallisation commences is about 1320° , the composition of the fused mass corresponding with 47% chromium. Alloys containing from 30–106% chromium undergo a change of structure at 1226° . The homogeneous mixed crystals which are primarily formed in the cooling process are transformed at this temperature into two different kinds of crystals, which are readily distinguished after electrolytic etching.

Cobalt and silicon are completely miscible in the liquid condition. In the solid state, the miscibility is confined to alloys containing less than 7.5% or more than 91% silicon. Five compounds are formed: Co_2Si , m. p. 1327° ; CoSi , m. p. 1393° ; CoSi_2 , m. p. 1277° ; CoSi_3 , m. p. 1307° , and Co_3Si_2 , which is formed in the solid state from the compounds Co_2Si and CoSi .

Measurements of the magnetic permeability of the alloys and the temperatures at which the magnetic qualities undergo changes have been made.

The paper concludes with a discussion of the relationships between the metals iron, cobalt, and nickel on the basis of the freezing-point diagrams of their principal alloys. A table is given showing the miscibility in the liquid states and the compounds formed in each case. The data show that in the liquid as well as in the solid state, the miscibility of nickel with other metals is greater than that of cobalt, which in its turn is greater than that of iron. Nickel also yields the greatest number of compounds, and iron the smallest number.

Jl. M. D.

Cobalt-Tin Alloys. S. F. SCHEMITSCHUSCHNY and S. W. BELYNSKY (*Zeitsch. anorg. Chem.*, 1908, 59, 364—370. Compare Lewkonja, preceding abstract).—The alloys formed by cobalt and tin have been studied by an investigation of the cooling curves of molten mixtures containing different proportions of the two metals, and an examination of the micro-structure of the solidified products. The freezing-point diagram, constructed from the experimental data, shows the existence of five curves. Two compounds, Co_2Sn and CoSn , are indicated. The former corresponds with a maximum freezing temperature of 1171° , the latter being characterised by a transition point at 927° . Above 515° , CoSn separates out in α -crystals, and below in β -crystals. The curves for the compounds are limited by eutectic points at 239° and 1112° . The eutectic alloy corresponding with 239° contains less than 1 atom % of cobalt, and that corresponding with 1112° , 79.5 atom % of cobalt. The two compounds are much harder than either of the components. The compound Co_2Sn is magnetic; CoSn has no magnetic properties either in the α - or the β -modification.

H. M. D.

Phosphorus Compounds of Nickel. N. KONSTANTINOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 742—752).—The freezing-point curve of nickel-phosphorus alloys indicates that, when melted together, nickel and phosphorus form the compounds Ni_3P_2 and Ni_2P , the former of which exists in two modifications; the β -form, which is stable at high temperatures, is transformed into the α -form at 1025° . At lower temperatures there exist also the compound Ni_3P , and another, richer in phosphorus than Ni_3P . With Ni_2P , the β -modification of Ni_3P_2 forms solid solutions, the limiting concentration of which corresponds with about 18% of phosphorus by weight (29.5 atomic %). These solid solutions decompose into the α -form of Ni_3P_2 and Ni_2P at 1000° .

T. H. P.

Action of Arsenic Trichloride on Nickel and the Arsenico-nickels. EMILE VILBOURX (*Compt. rend.*, 1908, 147, 426—428).—Powdered reduced nickel, when heated in arsenic chloride vapour, is not attacked below 400° . Between 400° and 600° , it is converted into nickel chloride and a compound having a composition corresponding with NiAs . The same compound is formed at 600° to 800° , but at 800° — 1400° the product consists of Ni_3As_2 .

By heating a mixture of powdered nickel and arsenic in an atmosphere of hydrogen, or by heating the metal in arsenic vapour, a series of arsenico-nickels is readily obtained. These contain, when prepared at 300° — 400° , 72% of arsenic; at 400° — 600° , 65% of arsenic; at 600° — 800° , 56% of arsenic; above 800° , 46% of arsenic, whilst an arsenide containing 39% of arsenic is obtained by treating alloys containing 11—38% with dilute sulphuric acid and separating with a magnet. On heating with arsenic chloride vapour, these arsenico-nickels tend to form NiAs at 400° — 800° by absorption or loss of arsenic, whilst at 800° — 1400° the resulting compound is Ni_3As_2 .

The arsenide NiAs , identical with the natural nickeline, has a red

colour, and, according to the temperature of preparation, is obtained as a powder, composed of small crystals with a metallic lustre, or as a slightly fritted mass, D^o 7.57.

The arsenide Ni_3As_2 (also obtained by Wöhler, *Ann. Chim. Phys.*, 1832, [ii], 51, 208; by Descamps, *Abstr.*, 1878, 705, and by Granger and Didier, *Abstr.*, 1900, ii, 349) is a grey, pulverulent substance with a metallic lustre, which melts at 1000^o , giving a hard, brilliant silver-white ingot, which readily breaks into lamellæ, D^o 7.86.

The arsenide $NiAs$ commences to lose arsenic at 100^o , being converted into Ni_3As_2 , which is very stable, and is only slightly decomposed at 1400^o . Conversely, when heated in an atmosphere of hydrogen at decreasing temperatures in the presence of arsenic, these two compounds absorb the latter, giving, finally, below 400^o a grey powder having the composition $NiAs_2$, identical with rammelsbergite.

The arsenides are attacked by heated chlorine, oxygen, or sulphur vapour. They are rapidly dissolved by nitric acid and aqua regia, are very slightly attacked by hydrochloric and sulphuric acids, are decomposed by fused potassium chlorate and nitrate, but are only slowly attacked by alkalis or alkali carbonates. E. H.

Some Alloys of Chromium and Manganese. G. HINDBRICKS (*Zeitsch. anorg. Chem.*, 1908, 50, 414-449).—Aluminothermic chromium and aluminium were used. Chromium is very viscous at its melting point, and requires to be heated more strongly to yield uniform alloys; magnesia crucibles are therefore necessary. When a carbon electric furnace is used, some carbon is always absorbed by the chromium, owing to the passage of gas through the porous magnesia.

The freezing point of chromium (1550^o) is lowered by the addition of tin up to 10^o , mixed crystals being formed up to 6% Sn. Beyond this, two liquid layers are formed, one of which is practically pure tin.

Chromium and copper are only miscible to a small extent in the liquid state, but the emulsion formed does not separate readily into two layers.

Liquid chromium and silver are also only partly miscible. The addition of 5% Ag lowers the freezing point of chromium by 50^o . Solid solutions are not formed.

Molten zinc dissolves chromium to some extent; molten cadmium not at all.

The addition of 25% of lead lowers the freezing point of chromium by 80^o ; alloys richer in lead separate into two layers, one of which is pure lead.

The preparation of alloys of chromium and aluminium is difficult, owing to oxidation and to the action of aluminium on the magnesia crucible at the high temperature necessary. It is better to prepare them by the ignition of a mixture of aluminium, chromium oxide, and potassium dichromate. Between 5% and 55% Cr, the liquid forms two layers, and there appears to be a compound of the formula Cr_2Al , the melting point of which lies much above 1600^o .

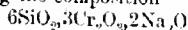
Manganese and silver form immiscible liquids from 30% to 90% Mn, and do not form solid solutions.

Manganese and aluminium form two compounds, probably Mn_3Al and $MnAl_3$, both of which form mixed crystals. Alloys containing between 57% and 86% Al separate into two liquid layers.

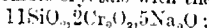
Tammann's rule (Abstr., 1907, ii, 445) is confirmed, that the element with the higher m. p. takes up more of that with the lower m. p. to form mixed crystals than conversely.

C. H. D.

Sodium Chromosilicates. ZYGMUNT WEYBERG (*Centr. Min.*, 1908, 519—523).—By fusing a mixture of silica, sodium carbonate, and chromic oxide with a large excess of sodium chloride, a dark green, crystalline powder having the composition



was obtained; the crystals are orthorhombic and strongly pleochroic. A mixture of sodium metasilicate, chromic hydroxide, and excess of sodium chloride gave rhombic crystals with the composition



and a mixture of ammonium dichromate, sodium metasilicate, and sodium chloride gave the product $95SiO_2 \cdot 2Cr_2O_3 \cdot 3Na_2O$ in tridymite-like crystals.

The compounds obtained when chromium takes the place of aluminium or iron in these experiments are thus of quite a different type (Abstr., 1906, ii, 23, 91, 865). When the sodium salts are replaced by salts of other alkali or alkaline earth metals, no definite results were obtained. With lithium salts, olivine-like crystals of lithium ortho-silicate, Li_4SiO_4 , were formed.

L. J. S.

Treatment of Pitchblende Residue. LUDWIG HAETINGER and KARL ULRICH (*Monatsh.*, 1908, 20, 485—496).—The paper deals with the working up of the radioactive residue (10,000 kilograms) from 30,000 kilograms of pitchblende containing 53.4% U_3O_8 . The operations, which occupied two years, are the following: The residue is heated for a working day with half its weight of sodium hydroxide (25% solution). After washing away the greater part of the soluble sulphates, the residue is digested on the water-bath with one and a-half times its weight of hydrochloric acid (1:1), and then washed with water. The hydrochloric acid extract is practically free from radium, but contains the bismuth-polonium and the actinium. The residue is next heated with half its weight of sodium carbonate (25% solution, free from sulphate), whereby a great part of the radium sulphate is converted into the carbonate; the mass is washed until free from soluble sulphates, and treated with pure hydrochloric acid. After three such treatments with sodium carbonate, &c., the final residue is practically free from radium, as also are the sodium carbonate extracts and the aqueous washings. The hydrochloric acid extracts, containing all the radium, are treated with sulphuric acid; the precipitated sulphates of lead, metals of the alkaline earths, and of the rare earths in the form of double sulphates, are heated repeatedly with an excess of concentrated sodium carbonate. The conversion of the sulphates into the carbonates is never complete, and therefore, after extracting

the mass with hydrochloric acid, the residue is boiled with water to remove the lead chloride (which is purified by recrystallisation and utilised for the preparation of radioactive lead) and then added to the next batch of crude sulphates. The hydrochloric acid solution, containing the radium, is freed from lead by hydrogen sulphide, evaporated to dryness, and the greater part of the calcium chloride extracted by concentrated hydrochloric acid. The resulting crude chloride, containing radium and barium, and also strontium, calcium, and small amounts of other substances, weighs 20 kilograms in a moist state; the least soluble constituent is the radium chloride. By repeated fractionation, it is separated into two parts, one (2 kilograms) containing nearly all the radium, and the other (11 kilograms) containing very little. The smaller part is again fractionated until the first crop of crystals is reduced to 9 grams. This crop is dissolved, freed from a little impurity by hydrogen sulphide, and separated in silica vessels into four subsidiary fractions and one "final" fraction, on which a determination of the atomic weight, by Richard's method for barium, gave the value 225, whilst the activity number was 27.2×10^6 . The activity numbers of the four subsidiary fractions are 17.0×10^6 , 6.1×10^6 , 2.5×10^6 , and 3.1×10^6 respectively. The total calculated amount of radium corresponds with 3.236 grams of anhydrous radium chloride of activity 27.2×10^6 .

A portion of the crude bromium was converted into the bromide, from which a "final" fraction of radium bromide was obtained. It weighed 0.5 gram, and after a year the weight had decreased to 0.389 gram. It was examined by Brill, who found that it lost 5.4% in weight when heated, gained 17.2% when heated in a current of hydrogen bromide, and contained 0.1792 gram of radium. The fact that radium bromide loses bromine by keeping is not generally known. C. S.

Physicochemical Researches on Tin. VII. ERNST COHEN (*Zeitsch. physikal. Chem.*, 1908, 63, 625—634. Compare Abstr., 1900, ii, 83, 212, 408; 1901, ii, 106, 214; 1904, ii, 567; 1905, ii, 168).—Since the publication of the author's earlier papers, numerous cases of the corrosion of coins, organ-pipes, and other articles made of tin, due to partial conversion into the grey modification, have come to light. Photographs of a number of these articles are reproduced.

A large quantity of grey tin having been put at the disposal of the author, the transition temperature has been determined with greater accuracy than heretofore. It is found to lie very close to 18°.

J. C. P.

An Alloy of Thorium and Nickel. ÉDOUARD CHAUVENET (*Bull. Acad. roy. Belg.*, 1908, 684—685).—Moissan and Hönigschmidt (Abstr., 1906, ii, 678), attempting to prepare metallic thorium by reducing potassium thorium chloride or thorium chloride with metallic sodium, obtained a metal containing 10—25% of thorium. The author, using lithium instead of sodium, and heating in a nickel boat, failed to prepare pure thorium, but obtained an alloy of thorium and nickel in the form of either grey lamellæ or a black pyrophoric powder. The analysis of this agrees with the formula Th_2Ni . The alloy in

variably contains 10% of thorium oxide. The pyrophoric variety inflames spontaneously either when powdered in a mortar or when dried in an oven at 115°. It does not give nickel carbonyl when heated in carbon monoxide at 60°, whilst at 400° the gas is decomposed with depositions of carbon. The alloy is non-magnetic, and is rapidly dissolved by hydrochloric acid.

E. H.

Rapid Preparation of Antimony Pentasulphide (Golder's Sulphide). ALBERT SARTORIUS (*Chem. Zentr.*, 1908, i, 2130—2131; from *Apoth. Zeit.*, 1908, 23, 342—343).—The usual method of preparing Schlippe's salt is to boil antimony trisulphide and sulphur with sodium hydroxide one and a-half to two hours, when, theoretically, sodium sulphantimonate and sodium meta-antimonate should be formed, if, however, the process is stopped after one-quarter of an hour's boiling, it is found that scarcely any of the antimony trisulphide has been acted on, the reaction that takes place being expressed by $6\text{NaOH} + 4\text{S} + 2\text{Na}_3\text{S}_2\text{O}_3 + 3\text{H}_2\text{O}$. To avoid this formation of thiosulphate, the author adds the mixture of antimony trisulphide and sulphur to the boiling sodium hydroxide solution, in small portions at a time. Under these conditions, the reaction proceeds according to the following equation: $4(\text{Sb}_2\text{S}_3 + 2\text{S}) + 18\text{NaOH} = 5\text{Na}_3\text{SbS}_4 + 3\text{NaSbO}_3 + 9\text{H}_2\text{O}$, and in a shorter time a larger yield of Schlippe salt of a better quality is obtained.

J. V. E.

Thioantimonates of Alkali Metals. II. A. D. DONK (*Chem. Weekblad*, 1908, 5, 629—645. Compare Donk, this vol., ii, 763).—From mixtures of the corresponding alkali thioantimonates with methyl alcohol and water, the following hydrated salts have been isolated: $\text{Na}_3\text{SbS}_4 \cdot 9\text{H}_2\text{O}$ (at 0° and 30°) and $\text{K}_3\text{SbS}_4 \cdot 9\text{H}_2\text{O}$ (at 15°). Similar mixtures of alkali thioantimonates with the corresponding hydroxides and water yielded the following hydrated salts:

$\text{Na}_3\text{SbS}_4 \cdot 9\text{H}_2\text{O}$; $\text{NaOH} \cdot \text{H}_2\text{O}$ (at 30°); $\text{K}_3\text{SbS}_4 \cdot 5\text{H}_2\text{O}$; $\text{K}_3\text{SbS}_4 \cdot 3\text{H}_2\text{O}$; $\text{K}_3\text{SbS}_4 + \text{KOH} \cdot \text{H}_2\text{O}$; $\text{KOH} \cdot \text{H}_2\text{O}$ (at 30°); $(\text{NH}_4)_3\text{SbS}_4 \cdot 4\text{H}_2\text{O}$ (at 30°); $\text{LiOH} \cdot \text{H}_2\text{O}$; $\text{Li}_3\text{SbS}_4 \cdot 10\text{H}_2\text{O} + \text{LiOH} \cdot \text{H}_2\text{O}$; $\text{Li}_3\text{SbS}_4 \cdot 10\text{H}_2\text{O}$ (at 30°).

A. J. W.

Dissolution of Metallic Gold in Hydrochloric Acid in Presence of Various Organic Substances. N. D. AVERKIEFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 840—859).—Metallic gold dissolves in hydrochloric acid in presence of the following compounds, which are arranged in decreasing order of effectiveness: methyl alcohol, amyl alcohol, chloroform, ethyl alcohol, chloral hydrate, phenol, sucrose, glycerol, trioxymethylene, formaldehyde. The dissolution takes place slowly at the ordinary temperature, but much more rapidly on heating, the time of heating having but little effect on the rate of solution. In some cases it was found that the solution of the gold was accelerated by increasing the amounts of acid and organic substance.

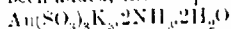
The residues obtained by evaporating these solutions on a water-bath give metallic gold on ignition, the loss on ignition differing from

that observed with $\text{AuCl}_3 \cdot 2\text{H}_2\text{O}$ (loss, 51.6%). Thus, with chloroform, this loss is 45.63; with methyl alcohol, 60.3; with phenol, 65.68; with ethyl alcohol, 78.0; with trioxymethylene, 85.1, and with amyl alcohol, 85.01%.

The results obtained indicate the existence of new compounds and reactions of gold, which are being further studied. T. H. P.

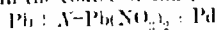
Complex Gold Sulphites. ARTHUR ROSENHEIM, JULIAN HERTZMANN, and MAX PRITZE (*Zeitsch. anorg. Chem.*, 1908, 59, 198—202).—Two complex sulphites of tervalent gold, $\text{K}_3[\text{Au}(\text{SO}_3)_4] \cdot 5\text{H}_2\text{O}$ and $\text{Na}_3[\text{Au}(\text{SO}_3)_4] \cdot 14\text{H}_2\text{O}$, were obtained in slender, deep yellow needles by the action of the corresponding alkali hydrogen sulphites on a solution of auric chloride in just sufficient alkali to form a clear solution. The compounds are stable in cold alkaline solution, but soon decompose in neutral or acid solution. On heating, the yellow alkaline solutions become colourless, and probably contain univalent gold, but no definite compounds could be isolated.

When a concentrated solution of gold chloride is added drop by drop to a solution of ammonium sulphite containing excess of ammonia, and the solution is gently warmed, it becomes colourless, and the compound, $\text{Au}(\text{SO}_3)_3 \cdot 4\text{NH}_3 \cdot 4\text{H}_2\text{O}$, separates in colourless, lustrous leaflets. Similarly, from a solution of potassium sulphite to which excess of ammonia has been added, the compound



is obtained in colourless needles. The constitution of these two compounds has not been established. G. S.

Nature of Palladium-Lead Alloys. NICOLAI A. PUSHIN and N. P. PASHKY (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 826—829).—The authors have prepared a number of alloys of palladium and lead by melting the metals in a mixture of lithium chloride with either potassium chloride or barium chloride. The potentials of the various alloys were measured by means of a $\text{Pb} - \text{X} - \text{Pb}(\text{NO}_3)_2$ alloy element (compare Pushin, Abstr., 1907, ii, 325). All the alloys containing less than 33% (atom.) of palladium have a potential practically identical with that of pure lead, whilst those containing more than 33% (atom.) of palladium give with pure lead a P.D. of more than 600 millivolts. Alloys of the latter class give at first a P.D. of 350—400 millivolts, which, however, increases rapidly at the commencement and more slowly later, approaching asymptotically the value 605—640 millivolts, which value persists for eight to ten hours. The potential of pure palladium also changes in the course of time, the element



having at first a P.D. of 760 millivolts; after two hours, the value 880 millivolts is reached, and after a further three hours, this begins to diminish slowly until 600 millivolts is reached. The above results prove clearly the existence of the compound Pb_3Pd . T. H. P.

Mineralogical Chemistry.

Native Tellurium from Asia Minor. GIUSEPPE CESÀRO (*Bull. Acad. roy. Belg.*, 1908, 255—257).—Amongst a series of specimens from the mines of Balıa was a large (2×3 cm.) dendritic crystal of native tellurium intergrown with quartz. A small proportion of gold is the only impurity present in the material. L. J. S.

Action of Potassium Chlorate on Pyrites and on Hauerite. (GIORGIO SPEZIA (*Atti. R. Accad. Sci. Torino*, 1908, 43, 728—734).—A mixture of pyrites with sufficient potassium chlorate to oxidise between 1 and 2 atoms of the sulphur of the pyrites explodes when brought into contact with either concentrated sulphuric acid or a flame. Under similar conditions, a mixture of sulphur or stibnite with potassium chlorate undergoes rapid combustion, approaching to explosion. With less or more than the above proportion of chlorate, pyrites gives a mixture which does not explode, but undergoes more or less rapid combustion.

The reaction between pyrites and potassium chlorate in the wet way differs, however, greatly from that between sulphur or stibnite and potassium chlorate. When the former mixture, either in explosive proportions or containing an excess of the chlorate, is heated with water, a vigorous reaction begins at 75° and continues without further heating; a yellow deposit forms, chlorine is evolved, and sulphuric acid is detectable in large proportion in the solution. A reaction also takes place very gradually in the cold, but in this case no evolution of chlorine is observed. With potassium chlorate and sulphur or stibnite, no such reaction occurs, and only after protracted heating at 100° is a trace of sulphuric acid formed.

Marcassite behaves with potassium chlorate, in both the wet and dry ways, in the same manner as pyrites, the vigorous reaction in the presence of water commencing at 70° . Hauerite forms an explosive mixture with potassium chlorate, but does not react with it in the presence of water, even at 100° .

When heated, hauerite begins to lose sulphur at about 170° , and is ultimately converted into manganese monosulphide; pyrites, on the other hand, loses sulphur only at about 350° , and gives a compound corresponding with pyrrhotite as final product, the monosulphide only being obtained from pyrites by heating in a current of hydrogen.

From these results, the author concludes that the sulphur present in combination with iron in pyrites has properties different from those of elementary sulphur.

T. H. P.

Natural Ferrous Oxide Hydrate. HARR (*Chem. Zeit.*, 1908, 32, 746).—In the clay deposit near Cuxhaven, hard, yellowish-brown lumps have been found among volcanic ash, which crumble when exposed to the air and appear to be ferrous oxide dihydrate, $\text{FeO} \cdot 2\text{H}_2\text{O}$.

Analysis showed 12.55% to be insoluble in hydrochloric acid; the soluble portion had the following composition :

FeO.	Fe ₂ O ₃ .	CaCO ₃ .	MgCO ₃ .	SO ₃ .	Water.	Total.
43.63	0.42	4.5	8.52	0.75	27.71	95.13

The powdered substance had D_{17.5} 3.205.

J. V. E.

Origin of the Boric Acid in the Solfioni of Tuscany.

RAFFAELLO NASINI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 43-46).—In a paper read before the Sixth International Congress of Applied Chemistry in Rome (1906) on "The Boraciferous Solfioni and the Boric Acid Industry of Tuscany," the author referred to a theory put forward by E. Perrone to explain the formation of these solfioni. This theory regards tourmaline as the source of the boric acid. The original temperature of the vapours of the solfioni cannot be less than 250°, and the depth from which they come must be from 5000 to 8000 metres. At this depth there probably exist granitic rocks containing tourmaline, having the characters of the granite found in Elba and elsewhere. The author's experiments show that when steam at a high temperature is passed over tourmaline extracted from Elba granite and subsequently condensed, the condensed liquid contains boric acid. As, further, this granite exhibits radioactivity, the presence of radioactive gases in the solfioni gases is readily explained.

Objections to this theory raised by D'Achardi (*Atti Soc. toscana sci. nat. Mem.*, 1907, 23) and Lotti (*Rassegna mineraria dell'ind. chim.*, 1907, 26, No. 11) are discussed.

T. H. E.

The Wide Distribution of Scandium in the Earth.

HARD (*Sitzungsber. K. Akad. Wiss. Berlin*, 1908, 851-868).—Although scandium appears to be relatively abundant in the sun and stars, yet it has only rarely been detected in terrestrial materials. Three-hundred and sixty-six samples of minerals, rocks, and meteorites of various kinds were examined spectroscopically, and traces of scandium found in a large number of them. It occurs most frequently in zirconium minerals, beryl, titanates, columbates, and titanocolumbates of the rare earths, in micas, and in tin and tungsten ores. Wolframite from Zinnwald, Bohemia, contains 0.2% of scandium oxide (Sc₂O₃).

L. J. S.

Composition of Parisite and Malacon. G. P. TSCHERNIA (*Vien. Zentr.*, 1908, ii, 192; from *Verh. Russ. Min. Ges.*, 1907, 44, 507-545).—The minerals analysed are from a weathered granitic granite from the neighbourhood of Mukden. The prismatic crystals of parisite are of two kinds: 1, dark grey and transparent, D 1.523, H 5-6; 2, yellowish-grey and opaque, D 1.531, H 4-5.

	CaO.	Li ₂ O.	Y ₂ O ₃ .	Fe ₂ O ₃ .	Al ₂ O ₃ .	Na ₂ O.	CO ₂ .	H ₂ O.	F.
I.	27.88	1.11	7.86	0.28	17.8	2.25	2.86	2.15	6.6
II.	27.81	1.02	8.76	0.30	24.5	2.94	2.9	2.6	6.6

The dark grey opaque grains of malacon, with D 1.016 and H over 7, gave the results under III:

	SiO ₂ .	SnO ₂ .	ZnO.	Fe ₂ O ₃ .	MnO.	Y ₂ O ₃ .	CaO.	H ₂ O.
III.	22.04	0.77	12.04	0.45	0.93	4.56	2.72	8.97

L. J. S.

Existence of a Monoclinic Soda Felspar, Isomorphous with Orthoclase. PHILIPPE BARBIER and A. PROST (*Bull. Soc. chim.*, 1908, [iv], 3, 894—899. Compare this vol., ii, 704).—Analyses of seven samples of orthoclase, briefly described in the original, show that orthoclases exist having the potassium partly or wholly replaced by sodium, the latter occurring as a special silicate (not identical with albite) which can ally itself with the orthoclase molecule without causing a change in crystalline form. If orthoclase is represented by the expression $K_2Al_2Si_6O_{16}$, the sodium compound must be represented as $Na_2Al_2Si_6O_{16}$.
T. A. H.

Kaersutite from Linosa and Greenland. HENRY S. WASHINGTON and FRED. EUGENE WRIGHT (*Amer. J. Sci.*, 1908, [iv], 26, 187—211).—Crystals of a black basaltic amphibole were collected from the tuff of a small parasitic cone of Monte Rosso, on the small island of Linosa off the coast of Tunis. They are monoclinic, with a prism cleavage angle of $55^{\circ}22'$. Thin sections are brown and strongly pleochroic; the extinction angle is small and in the acute angle β (on the prism plane $c':c = +1.4^{\circ}$); the optic axial plane lies in the plane of symmetry, and $2V$ is about 80° . Analysis I shows the mineral to be highly titaniferous, and to be very similar to the kaersutite (of Lorenzen, 1884) from Kaersut, in Greenland. A re-examination and a new analysis (II: 0.77% apatite deducted) were made of the original kaersutite:

	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	NiO	MgO
I.	49.85	8.47	9.89	8.85	3.36	0.12	0.19	12.47
II.	39.52	10.31	11.22	7.22	8.81	0.06	nil	19.31
	CaO	Na ₂ O	K ₂ O	H ₂ O	F	Total	Sp. gr.	
I.	12.16	2.01	0.63	0.19	0.28	99.98	3.336	
II.	19.93	2.95	1.07	0.59	—	100.00	3.147	

The presence together of large amounts of titanium and iron oxides (Fe_2O_3 and TiO_2 or FeO and Ti_2O_3) gives rise to uncertainties in the analyses and in the interpretation of the results: the results can, however, be made to conform with the meta-silicate formula of Penfield and Stanley (Abstr., 1907, ii, 102).
L. J. S.

Mineralogy of Sardinia. II. A. PELLICCINI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 70—74. Compare *Atti R. Accad. Lincei*, 1904, [v], 13, ii).—The author describes crystals of idocrase found (1) in the Baccu Arrodas Mines in Sarrabus, and (2) in the Rio Planu Castangias Mines in Iglesias.

[CARLO RIMATORI.]—The composition of the crystals from Rio Planu Castangias is as follows:

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	Total	PE.
39.17	11.35	13.39	33.31	11.60	11.60	3.74	109.96	3.358

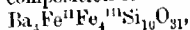
T. H. P.

Taramellite, a New Silicate of Iron and Barium. E. TACCONI (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 810—814; *Cento Min.*, 1908, 506—508).—The author describes a new mineral, taramellite, occurring

in radiating, fibrous, acicular aggregates or slender veins in the crystalline, calcareous zone of Candoglia-Ornavasso (Val Tcece), where it is found in intimate association with magnetite, pyrites, chalcopyrite, paracelsian, pyroxene, and amphibole. It has a reddish-brown colour, a silky or fatty lustre, a hardness of about 5.5, D^{25}_D 3.023, n greater than 1.74. The mineral exhibits distinct pleochroism, and has the composition :

SiO ₂	Fe ₂ O ₃	FeO.	BaO.
36.56	21.51	4.47	37.32

together with traces of titanium, aluminium, manganese, and magnesium. The above composition leads to the formula



and the mineral may be regarded as a basic salt of a polymeride of metasilicic-acid, $\text{Ba}_4\text{Fe}^{11}(\text{Fe}^{10}\text{O})\text{Fe}_3(\text{SiO}_3)_{10}$. T. H. P.

The Zeolites of Montresta (Sardinia). LUCIANO PELACANI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 66—70).—The zeolites of Montresta include mesolite (anal. I), chabazite (anal. II), heulandite, and stilbite, the first occurring in greatest, and the last in smallest, proportion :

	SiO ₂	Al ₂ O ₃	CaO.	Na ₂ O.	K ₂ O.	H ₂ O.	Total.
I.	42.01	25.05	19.87	8.12	trace	15.32	100.39
II.	46.30	21.96	7.78	—	2.27	21.37	99.68

The analyses agree with those of Rimatori (Abstr., 1900, ii, 735). Mesolite is regarded as an isomorphous mixture of scolecite and natrolite, and, from a study of the emission of water on heating, the mesolite of Montresta seems to be more closely allied to scolecite than to natrolite. The amount of water emitted by chabazite when gradually heated to 350° increases more slowly than the temperature rises, whilst with mesolite the reverse is the case. The reabsorption of the water removed by heating to 350° takes place rapidly and completely with chabazite, whilst with mesolite it is slow and only partial. After heating to redness, chabazite absorbs about one-fourth of the total water emitted, whilst mesolite absorbs none at all.

The heulandite has the composition :

SiO ₂	Al ₂ O ₃	CaO.	SiO ₂ & BaO.	Na ₂ O.	K ₂ O.	H ₂ O.	Total.
47.72	15.69	7.62	14.68	2.87	trace	15.77	99.34

which approximates to that of the heulandite from Beaunord, analysed by Rammeisberg (*Zeitsch. deut. geol. Ges.*, 1869, 21, 93). The stilbite was found only in small quantity, insufficient for analysis. T. H. P.

New Vein of Nephelitic Basalt containing Noseite (Nosean) in Vincentino. L. MADDALENA (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 802—809).—The author has discovered in Vincentino a nephelitic basalt of microporphyrific structure, containing pyroxene, biotite, apatite, magnetite, and noseite, the last being scattered irregularly in

crystals and granules, mostly of hexagonal habit. The basalt has the composition :

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.	Na ₂ O.	K ₂ O.
31.39	12.15	5.89	6.41	0.41	16.61	9.82	3.48	1.21
P ₂ O ₅ .	TiO ₂ .	CO ₂ .	H ₂ O at 110°.	H ₂ O at red heat.	Total.			
1.40	1.23	5.31	1.66	3.17	100.14			

which approximates to that of the basalt of Recoaro, the lower proportion of silica in the Vincentino basalt being due to the more advanced condition of alteration of the rock. T. H. P.

Physiological Chemistry.

Regulation of Respiration. F. H. SCOTT (*J. Physiol.*, 1908, 37, 301—326).—The respiratory mechanism may be stimulated by small amounts of carbon dioxide, or by great diminution of oxygen in the inspired air. These produce increase of both rate and depth of breathing, but if the vagi are divided, the depth increases but not the rate. The alveolar tension of carbon dioxide rises with rise of body temperature; the effect of vagal division on the tension is very variable. Inflation of the lungs even at the height of dyspnea inhibits inspiration, but if the vagi are divided, it has no effect. The effect of repeated ventilations depends on the washing-out of carbon dioxide from the blood (confirmatory of Haldane). The vagi in reference to respiration are regarded in the same light as the sensory nerves of muscle; without these nerves muscular movements are excessive, and thus resemble those of an ataxic limb. W. D. H.

Heart Perfusion Apparatus. THOMAS G. BRODIE and WINIFRED C. CULLIS (*J. Physiol.*, 1908, 37, 337—349).—A new apparatus for the perfusion of the isolated mammalian heart is described and figured. W. D. H.

Hæmagglutination and Hæmolysis. LEO VON LIEBERMANN (*Centr. Bakt. Par.*, 1908, 47, ii, 372—378).—Polemical and theoretical. Von Eisler (*Centr. Bakt. Par.*, 1908, 46, 355) has attributed to the author the view, that agglutination by ricin is due to the acid nature of this substance, pure and simple. This is a misunderstanding; ricin appears, indeed, to be an acid, but its agglutinant action is a specific property, not shared by other acids, and due to the peculiar physical properties of the ricin-stroma combination (compare Abstr., 1907, i, 573). In connexion with this, Landsteiner's views are discussed. The inhibitory action of alkali primarily extends to the complement, but also affects the immune substance. G. R.

The Time Relations of Haemolysis on Exposure to Light of Sensitised Red Blood-corpuscles. O. HÄRZBECKER and ALB. JODLBAUER (*Biochem. Zeitsch.*, 1908, 12, 306—313).—Suspensions of red blood-corpuscles were submitted to the action of the sensitising substances eosin and sodium dichloroanthracenedisulphonate in the dark, and then exposed to light. The amount of haemolysis was ascertained by measuring the volume of blood-corpuscles, and of haemoglobin in the supernatant liquid, in samples of liquid centrifuged after different intervals of exposure to light. It was found in all cases that haemolysis was a gradual process, and took place at the same rate whether the fluorescing substance was within or both within and without the cell.

S. B. S.

Haemolysis by Snake Poison. von DUNGERN and COCA (*Biochem. Zeitsch.*, 1908, 12, 407—421).—The haemolytic action of cobra poison depends entirely on the existence of a lipolytic enzyme, by means of which haemolytically-acting scission products, especially deoleo-lecithin and oleic acid, are produced. Compounds of lecithin and cobra toxin do not exist; there are no such substances as either saturated or unsaturated toxolecithides. The preparations of Kres (Abstr., 1907, ii, 569) are mixtures of ferment with deoleo-lecithin, contaminated with other substances, or their scission products, which are found in commercial lecithin. Cobra poison contains no amboceptors, and the haemolysis produced by a combination of cobra poison and complement containing serum is due to a complex serum haemolysin, which acts haemolytically only under certain conditions, and only when the blood-corpuscles have taken up a certain quantity of lipase.

S. B. S.

Haemolysis by Soaps, and the Relationship between Soaps and the Complex Haemolysins of the Blood-serum. MAX FRIEDMAN and FRITZ SACHS (*Biochem. Zeitsch.*, 1908, 12, 259—271).—Noguchi and von Liebermann have shown that soap can be deprived of its haemolytic properties by admixture with serum, and have expressed the view that this inactivated mixture acts as a complement, the haemolytic powers of which can be called into play by the addition of an amboceptor. Such an amboceptor, von Liebermann claims to have discovered in oleic acid. The authors have devised experiments to test the above hypotheses. They have confirmed the fact of the combination between serum and the soap, which is rendered more stable by heating to 70°. They have, however, been unable to confirm the hypotheses as to the complement nature of this combination, or of the amboceptor nature of oleic acid. The activation of the amboceptor by the addition of the soap-serum mixture, they ascribed to the action of a true serum complement contained in the sera, which had not been entirely destroyed by heating to 50°. The supposed amboceptor action of oleic acid they ascribed to the additive action of the acid and of the soap-serum mixture, each of which was, by itself, unable to produce haemolysis.

S. B. S.

Haemolysis by Soaps. FRITZ SACHS (*Biochem. Zeitsch.*, 1908, 12, 278—289).—Although soaps can be deprived of their haemolytic power

by previous admixture with serum, the latter can accelerate their action if the soaps be added first to the suspension of corpuscles. Serum can also accelerate in a like manner, the hemolytic action of oleic acid, which fact, amongst others, led von Liebermann to ascribe amboceptor functions to this acid. The author has attempted to determine the nature of the substance in serum which accelerates hemolysis by soaps. Serum-albumin is inactive; alkalis markedly accelerate the action. It is not to the alkali, however, that serum owes the accelerating property, for neutralised or dialysed serum still possesses it; furthermore, serum which has been deprived of its proteins loses this property. Serum which has been extracted with ether, gains in the hemolysis-accelerating power. The experiments with alkali render it probable that the concentration of hydroxyl ions influences the hemolysis, and the extraction of serum by ether, in removing the fatty acids from the soaps contained therein, may increase the alkalinity of the serum. The experiments, however, lead to no definite conclusions as to the nature of the hemolysis-accelerating substances in serum.

S. B. S.

The Point of Attack of Photodynamic Substances in Paramoecia. HERMANN VON TAPPEINER (with F. OSTHEIDER and E. ENLARDT) (*Biochem. Zeitsch.*, 1908, 12, 290—395).—*Paramoecia*, which have been treated with eosin in the dark, are no more strongly sensitised than those which have been exposed immediately to the light. The eosin does not appear to possess the property of penetrating the cell; its action in sensitising is entirely at the periphery. Dichloro-anthracenedisulphonic acid and methylene-blue, on the other hand, are taken up in active form by the cell in the dark; their point of attack is intracellular; there is evidence, however, in the case of these two substances of a peripheral, in addition to the intracellular, action. As to the nature of the peripheral action, nothing definite can be stated.

S. B. S.

Action of Fluorescent Substances on Red Corpuscles. HERMANN VON TAPPEINER (*Biochem. Zeitsch.*, 1908, 13, 1—23).—Eosin and sodium dichloroanthracenedisulphonate produce in the dark at the room temperature no noteworthy destruction of red corpuscles, and, after removal from the solution, they undergo hemolysis at 39° at the same rate as untreated corpuscles. In the light, however, rapid hemolysis occurs. These substances are therefore taken up by the corpuscles in a form in which they are not sensitised. This hemolysis is more rapid if the light acts before than after washing of the corpuscles from the fluorescent solution. Whether the action occurs in the interior or on the surface of the corpuscles is discussed; phenosafranine shows both kinds of action; methylene-blue only a surface action.

W. D. H.

Action in the Dark of Fluorescent Substances on Proteins, Toxins, and Ferments, and its Reversibility. T. KUDO and ALB. JODLAUER (*Biochem. Zeitsch.*, 1908, 13, 24—43).—Many fluorescent substances act in the dark on the alexin of serum and on tetanolyisin, inhibiting their specific actions. This is not the case with

all fluorescent substances, and the concentration necessary to produce the effect in the dark is relatively high in comparison with that of those which act photodynamically. Those which act in the dark are considered to be adsorbed, and the action is reversible; the presence of alkali is favourable, whilst that of invertase, inhibits. W. D. H.

Nucleoli of *Hydra fusca*. C. E. WALKER and ALICE L. EMBLETON (*Quart. J. Exp. Physiol.*, 1908, 1, 287—290).—The observations relate to the movements of the nucleoli of the cells of the hydra from the nucleus into the surrounding cell protoplasm. The phenomenon is not related to cell division, but is connected with or dependent on metabolic changes, especially with digestion, since it is seen principally in endoderm cells. A marked change takes place in the staining reactions of the extruded nucleolus, which suggests that it undergoes an important chemical or physical change. W. D. H.

The Death of Leucocytes. The Vacuolation of Leucocytes. H. C. ROSS (*J. Physiol.*, 1908, 37, 327—332, 333—336).—Methylene-blue kills cells; it is not until death occurs that the nucleus is stained; this is hastened by heat and alkalis, and delayed by neutral salts. After death, the cytoplasm liquefies, and the granules show Brownian movements; this may be brought about by the absorption of fluid. During life the cytoplasm is a jelly.

Certain spots in leucocytes described by previous observers as centrosomes are droplets of fluid absorbed by the cells, which are suspended in the jelly-like cytoplasm. With the liquefaction of the latter which occurs on death, these droplets disappear. W. D. H.

The Production in vivo and in vitro of Precipitins for Ovalbumin by means of Antigens of a Chemically definite Nature. ANDRÉ MAYER and GEORGES SCHLEFFER (*Compt. rend.*, 1908, 147, 311—313).—The precipitating serum for egg-albumin, usually produced from the rabbits by repeated injection of egg-albumin into the animal, can also be obtained if the animal is starved for five or six days, and the serum collected when it has lost about one-third of its weight and the urine is markedly acid. The precipitating property also appears after chloroform intoxication, and after the formation of aseptic peritoneal abscesses by turpentine. In every case the serum loses its precipitating property after warming to 60°. It was assumed that precipitating sera were produced by the presence therein of products of tissue degradation. Amongst such products are the fatty acids, and attempts were made to produce precipitating sera by injection of these acids. It was found that the sera of animals which had received repeated injections of propionic, butyric, valeric, hexoic, and oleic acids produced marked precipitins with solutions of egg white. No precipitants were produced by the injections of octoic, stearic, palmitic, hydrochloric, lactic, or succinic acids.

The precipitate produced is specific for egg-albumin, and the precipitate is soluble in excess of either of the reacting substances; the serum also loses its precipitating properties on warming to 60°.

Soaps and ethyl esters on injection also produce precipitating sera, but the action is not so marked as in the case of the free acids.

Precipitating sera have also been obtained by adding directly to sera (without injection into animals) fatty acids, soaps, and ethyl esters. In the first case, which yields the most marked results, the precipitating property is only destroyed with difficulty by heating.

S. B. S.

Chemico-physical Studies of Animal Fluids. Ia. Viscosity of Blood-serum of Different Marine and Terrestrial Animals. FILIPPO BOTTAZZI (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 707—717).—Measurements are given of the time of outflow of the blood-serum of different animals from an Ostwald viscosimeter, compared with the values obtained with distilled and sea-water at the same temperatures.

W. A. D.

Chemico-physical Investigations on Animal Liquids. Ib. Viscosity of the Blood-sera of Certain Marine and Terrestrial Animals. FILIPPO BOTTAZZI (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 792—802. Compare preceding abstract).—The classification of marine and terrestrial animals according to the increasing time of efflux of their blood or body-fluid from a viscosimeter does not correspond with the ordinary zoological classification, so that the viscosity of the blood-plasma is not strictly dependent on the degree of organisation of the animal. The viscosity of the body-fluid of the marine invertebrates is only slightly greater than that of sea-water. The blood of cephalopods is distinguished from that of all other animals, vertebrate and invertebrate, by having the greatest viscosity. The viscosity of blood-serum increases with the proportion of colloids (sero-proteins) present.

T. H. P.

Chemico-physical Investigations on Animal Liquids. II. Content of Protein Nitrogen in the Blood-sera of Various Animals. FILIPPO BOTTAZZI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 16—26. Compare preceding abstracts).—The author has determined the proportions of nitrogen, precipitable by tannic acid, present in the blood-sera of various animals. The results show that, in this respect, marine and terrestrial animals are divided into four groups: (1) Those having sera or body-fluids containing less than 0.5% of protein nitrogen; this class includes *Siphunculi*, *Aplysia*, and probably, also, other low marine invertebrates. (2) Various vertebrates and invertebrates, including decapod crustaceans, birds, frogs, and the *Salicini*, with content of protein nitrogen varying from 0.52 to 0.67%. (3) Those with 0.8 to 0.9% of protein nitrogen, namely, herbivorous and carnivorous domestic mammals, such as cats, dogs, rabbits, and oxen. (4) Cephalopods, the serum of which contains, on an average, 1.66% of protein nitrogen. For the buffalo, the % of protein nitrogen is 1.3636, and for the pig, 1.230.

On comparing the numbers obtained with the viscosity results (see preceding abstract), it is found that, in general, the content of protein in the liquids examined increases with the viscosity. It is hence con-

cluded that the greater or less viscosity of the blood-plasma is due to the greater or less proportion of proteins present. This result is confirmed by experiments, in which the concentration of proteins in serum is increased artificially.

T. H. P.

Chemico-physical Investigations on Animal Liquids. III. Variations of Electrical Conductivity, Viscosity, and Surface Tension of Blood-serum during Dialysis. FILIPPO BOTTAZZI, G. BUGLIA, and A. JAPPELLI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 49—57. Compare preceding abstracts).—The electrical conductivity and surface tension of blood-serum diminish considerably during dialysis, the diminution being at first rapid and afterwards slow; the same is the case when the serum is filtered before the conductivity or surface tension is measured. The viscosity of the serum diminishes if the liquid is filtered before determining the time of efflux; here, too, a slight increase in the time of efflux is observable at the beginning of the dialysis. The diminution of the conductivity is evidently due to the diffusion of the electrolytes, and this also causes the precipitation of the seroglobulin.

T. H. P.

Action of Manganese and Iron Sulphates on Diastatic Ferments. ALFRED GIGON and T. ROSENBERG (*Chem. Zentr.*, 1908, ii, 84; from *Skand. Arch. Physiol.*, 1908, 20, 423—431).—A 1—2% solution of starch and a small quantity of manganese or iron sulphate were added to a freshly-prepared blood-serum, and the amount of sugar estimated by the polarimeter. The presence of these salts undoubtedly increases the amylolytic action of the blood-serum diastase, and is also favourable to the amylolytic ferment of the pancreatic juice.

J. V. E.

Chemistry of Digestion in Animals. XVII. Digestion and Absorption of Proteins Rich in Bases. E. S. LONDON (*Zeitsch. physiol. Chem.*, 1908, 56, 378—383). **XVIII. The Importance of the Mouth in Gastric Digestion.** E. S. LONDON and J. H. PEWSEYER (*ibid.*, 384—387). **XIX. Digestion and Absorption of Meat in the Intestine.** E. S. LONDON and TH. SULIMA (*ibid.*, 388—393). **XX. Laws of Digestion and Absorption in the Alimentary Tract.** E. S. LONDON and F. SANDBERG (*ibid.*, 394—403). **XXI. Further Investigations of the Same Laws.** E. S. LONDON (*ibid.*, 404—407). **XXII. The Importance of the Blood in Gastric Digestion.** N. A. DOBKOWOL-KAJA (*ibid.*, 408—416). **XXIII. Digestion and Absorption of Carbohydrates.** E. S. LONDON and W. W. POLOWOWA (*ibid.*, 512—544). **XXIV. Fat-splitting in the Alimentary Canal.** E. S. LONDON and M. A. WERSHOWA (*ibid.*, 545—550). **XXV. Composition, Digestion, and Absorption of Tubercle Bacilli.** E. S. LONDON and E. RIWKIND (*ibid.*, 551—553. Compare this vol., ii, 50).—The experiments were made on the dogs described in previous publications.

XVII.—If proteins, such as gelatin or histone (from the thymus) which are rich in bases are given, the products of digestion in the

jejunum and ileum contain only small amounts of free arginine. The chief substances obtained in the material issuing from the fistula are complexes which are precipitable by tannin. Absorption of gelatin occurs chiefly in the lower parts of the small intestine, and at the end of that tube it is fairly complete.

XVIII.—Details are given of the rate with which the stomach empties itself in dogs; this probably runs *pari passu* with the rate of digestion. Outside psychical influences do not affect this, but if the food is given by the mouth, it is much accelerated, probably because the normal reflexes due to taste impulses are set in motion.

XIX.—In flesh-feeding (200 grams), the total quantity of chyme which passes the various sections of the intestine decreases with each hour of the digestion period. The intervals between the peristaltic propulsions of the chyme are diminished by removal of the pylorus. The chyme is always a thick fluid, although its chemical and physical characters vary as it passes along; it also varies in the concentration of the digestion products in different segments of the intestine.

XX.—An attempt is made to construct mathematical formulae to show the relationships between the digested, undigested, and absorbed portions of the food in relation to its quantity and the quantity of juices secreted. The experiments on which these are based were made with gliadin as the food.

XXI.—Similar experiments with white of egg; although this is more difficult to digest than gliadin, the same general laws are stated to hold.

XXII.—Loss of blood delays digestion; loss of one-third of the total volume of blood stops it for three hours; during this time the fall of blood-pressure persists. The quality of the blood is also important; in hydraemia there is diminution of gastric activity.

XXIII.—Starch, dextrin, sucrose, and dextrose are not absorbed in the dog's stomach in any concentration, whether dissolved in water or alcohol. Of these carbohydrates, only sucrose and erythro-dextrin undergo slight fission (2–4%) in the stomach, and this is due to the acid, not to enzymes; still large quantities of gastric juice are secreted. No formation of lactic acid was observed. In the duodenum, the carbohydrates undergo fission, the amount of which stated numerically varies in the case of different carbohydrates. Absorption has its main seat in the jejunum and upper ileum; again, the amount is stated numerically. Absorption is completed in the lower ileum; this is usually 100% or nearly that. Only in the case of dry starch does any important amount (22%) pass through into the large intestine. The intestinal juice appears to be the main agent in the fission of carbohydrates; in starch digestion, however, the duodenal juice is of special importance. This intestinal activity leads to an increase of nitrogenous metabolism, which chiefly shows itself in the secretion of nitrogenous substances into the intestinal lumen.

XXIV.—The fission of emulsified fat begins in the dog's stomach soon after feeding, and reaches about 32%. This is partly due to gastric lipase, and partly to regurgitated duodenal contents. The pancreatic juice in the duodenum acts vigorously, cleaving 41% of the fat. Below this in the small intestine the percentage of free fatty

acids reaches its maximum, this in some portions reaching 95%; 69% of the fatty acids are still present in the large intestine.

XXV.—The main protein constituent of the tubercle bacillus approaches in composition those proteins with a mean percentage of diamino-acids. In the upper segments of the alimentary tract, it is digested, and it is absorbed throughout the length of the intestinal canal. In the lower ileum very little digestion of this protein takes place.

W. D. H.

Gastric Digestion in Fishes. M. VAN HERWERDEN (*Zeitsch. physiol. Chem.*, 1908, 56, 453–494).—This investigation definitely proves that the acid of the gastric juice in Selachian fishes is hydrochloric acid. An unimportant amount of formic acid is also present. The results in teleostean fishes are not so clear, mainly owing to the difficulty of collecting the juice during life. During digestion in selachians, the percentage of the acid may rise to 0.4. The proteolytic ferment present is probably pepsin, although some digestion may occur in a neutral medium, and in some teleostean fishes even in an alkaline medium. The acid is secreted at the cardiac region only of the stomach, but the epithelium differs from that seen in higher vertebrates. An amylolytic ferment is absent, but lipase is present.

W. D. H.

Influence of Bromine on Gastric Secretion. TOGAMI (*Biochem. Zeitsch.*, 1908, 13, 112–120).—Experiments on dogs with a Pavlov's "small stomach" show that aqueous solutions of bromine (in contradistinction to iodine) paralyse the stomach glands without any preliminary stimulation. Sodium bromide and bromo-protein compounds act, but not so constantly, in the same direction.

W. D. H.

[Importance of Calcium Salts for the Growing Organism.] ARNOLD ORGLER (*Biochem. Zeitsch.*, 1908, 12, 331–335). Compare this vol. ii, 696.—Explanation of a misunderstanding of the meaning of the term "balance" in a work by Aron and his collaborators (this vol. ii, 298), and criticised by the writer of the note.

S. B. S.

Behaviour of Lecithin with Bile Salts, and the Occurrence of Lecithin in Bile. JOHN H. LONG and FRANK GERHART (*J. Amer. Chem. Soc.*, 1908, 30, 1312–1319).—Some authors have stated that bile contains small quantities of lecithin, whilst others have expressed the opinion that this substance is absent. Hammarsten (*Abstr.*, 1901, ii, 529; 1903, ii, 86; 1904, ii, 831), whilst leaving the universal occurrence of lecithin in bile an open question, asserts that it is present in the bile of the polar bear.

Experiments have now been made with ox bile and with human bile, but lecithin could not be separated. It has been found that the bile salts, as usually obtained, carry down a phosphorus complex, which has been regarded by Hammarsten and others as a lecithin. This complex could not be completely removed from the bile salts, as the latter retain it very tenaciously.

Bile salts are capable of dissolving 80% of their weight of egg-lecithin, and much of this can be precipitated with acetone, but a small quantity remains with the bile salts, and is probably much greater than that contained in any bile. The addition of inorganic salts hastens the solution of lecithin by bile salts, but does not increase the amount dissolved. A few inorganic salts, however, such as aluminium and ferric chlorides and lead nitrate, cause the precipitation of the bile acids. When lecithin is dissolved in bile salts, the optical activity is increased, whence it is calculated that the lecithin has $[\alpha]_D + 7.75^\circ$.

E. G.

Action of Acids and Rennet on Human Milk. ENGEL (*Biochem. Zeitsch.*, 1908, 13, 89—111).—Hydrochloric, lactic, oxalic, and sulphuric acids precipitate human milk, and the optimal acidity is 2–3 c.c. of *N*/10 acid to 10 c.c. of milk. Phosphoric and acetic acids act best at a greater concentration (5 c.c.); the substance precipitated is caseinogen; rennet precipitates a calcium compound of this protein, and the amount necessary varies within wide limits, but the precipitation is most complete when combined with the optimal concentration of acid.

W. D. H.

Fat and Ester Hydrolysis in Tissues. PAUL SAXL (*Biochem. Zeitsch.*, 1908, 12, 343—360).—In organs containing only their own fat, or with additional added neutral fat, only a small amount of fat hydrolysis takes place during autolysis with exclusion of bacterial action. In the case of the addition of monoacetin, monobutyrin, and ethyl butyrate to organs, the increase of acidity after twenty-four to forty-eight hours is due, at any rate partly, to the formation of acid products of autolysis. Amyl salicylate is, however, hydrolysed by all the organs investigated, with the exception of muscular tissue. The power of ester hydrolysis generally is smaller in the case of the muscles than in all other organs. The hydrolysing power of blood-serum is also small. Phosphorus poisoning does not activate a lipase. None of the methods hitherto employed for determining the fat-hydrolysing power of tissues is quite trustworthy; the quantities of acid formed are too small after short periods of incubation to allow an accurate estimation of their quantity to be made, and the product of autolysis and other circumstances interfere with the correct estimation after longer periods. Any conclusions as to the lipase content of organs under pathological conditions must therefore be accepted with reserve.

S. B. S.

Inositol in Animal Tissues and Fluids. FRANZ ROSENBERGER (*Zeitsch. physiol. Chem.*, 1908, 56, 373—377).—A new method of extraction is described which avoids the faults of Scherer's older method. Fresh flesh contains no inositol (cyclitol); it is formed on keeping from a substance named *inositogen*. Ox-blood is free from both substances. Inositogen appears in the human placenta at the sixth month of foetal life; it is present in fresh eggs. The normal urine of men and dogs contains traces of inositol; that of the rabbit does not. The bodies of rabbits after inanition do not form inositol.

W. D. H.

Muscular Contraction and Receptive Substances. III. JOHN N. LANGLEY (*J. Physiol.*, 1908, 37, 285—300).—The present experiments deal with the action of nicotine on denervated frog's muscles. Up to 100 days after nerve-section, the local punctiform application of nicotine to the muscles causes tonic contraction, as it does in normal muscles; more dilute solutions cause fibrillary twitchings, for this purpose, however, a somewhat stronger solution is required than in normal muscles. It is therefore certain that nicotine produces its effects on muscle and not on nerve-endings. Possibly the contractile molecule of the muscle fibre has a number of receptive side-chains; combination of one of these with nicotine causes one effect, with another, the other effect. Curare prevents nicotine from causing contraction in muscles, whether denervated or not.

W. D. H.

The Physiology of the Glands. IX. The Relationship between the Hourly Excretion of Nitrogen and Resorption from the Intestine, and its Dependence on Rest, Work, and Diuresis. ERNST HAAS (*Biochem. Zeitsch.*, 1908, 12, 263—247).—The hourly output of urine and its nitrogen content were estimated after meals containing known amounts of nitrogen, when the subject of the experiment was doing muscular work, when at rest, and when excessive diuresis was produced by drinking large amounts of tea. The curves representing the output were of a fairly constant form. They showed as a rule three maxima, the first in the second hour, the second in the fifth, and the last in the seventh hour. The first maximum is due to a washing-out of nitrogenous metabolism products owing to the introduction of liquids in the meal; the second and third are due to the resorption of the ingested nitrogenous matter from the intestine. Work or rest have no definite influence on the amount of excreted nitrogen in the first eight hours after a meal. With increased diuresis, there is to a certain extent an increased nitrogenous excretion, which is due, not to increased protein decomposition, but to the washing-out of nitrogenous metabolites already existing in the organism. If the diuresis be brought about before the ingestion of a meal, a smaller quantity of nitrogen is subsequently excreted; this quantity under the conditions of experiments performed was a constant, and amounted to 65% of the nitrogen of the ingested food.

S. B. S.

The Elimination of Non-dialysable Substances by the Urine under Normal and Pathological Conditions. ULRICH EDECKER (*Biochem. Zeitsch.*, 1908, 12, 485—498). The amount of non-dialysable substance excreted in the urine depends on the amount of substance metabolised. In normal men it varies between 0.870 and 2.355 grams per day averaging about 1.44 grams. These numbers are markedly higher than those found for females (about 0.8 gram per day). They are also higher than the numbers found in cases of nervous diseases, and of chronic disturbances of the digestive functions. On the other hand, in cases of increased metabolic processes, even with decreased ingestion of food, such as in cases of

fever and diabetes, the reverse is the case. The residue, in normal cases, gave, when tested with the majority of the protein reagents, negative results; on hydrolysis with hydrochloric acid it yielded a reducing substance; probably it consists of chondroitinsulphuric acid and nucleic acid. In the case of pneumonia, however, appreciable quantities of a peptone appeared to be present. In composition, this substance was not far removed from that of the mucin of bronchial mucous membrane, and it yielded on hydrolysis a reducing substance. It is possibly a glucopeptone. S. B. S.

Colloid Nature of Pigments in Relation to their Behaviour in the Frog's Kidney. RUDOLF HÖBER and S. CHASSIN (*Zeitsch. Chem. Ind. Kolloide*, 1908, 3, 76—80).—The experiments described previously (this vol., ii, 716) are extended to twenty-one other dyes. The experiments lead to the following rules: (1) When a dye is not taken up by the kidney epithelial cells it is highly colloidal. The converse is not true, since some colloids are taken up, for example, Biebrich-scarlet, acid-violet, and aniline-blue. (2) When a dye has little or no colloid character, it is readily taken up. T. E.

A Colour Reaction of. Pathological Urine. OTTO GAUFF (*Biochem. Zeitsch.*, 1908, 13, 133—141).—Strzyzowski described in diabetic urine a reaction dependent on the amount of acetoacetic acid, the presence of which indicates a bad prognosis; it consists in the appearance of a green fluorescence at room temperature within twenty-four to forty-eight hours when formaldehyde is added to the urine. In the present research, it is shown that the prognosis is not necessarily bad, and that the reaction is not specific for diabetic urine, but is found in a large number of other diseases. Ammonia is increased as well as acetoacetic acid in the urine, and a mixture of ammonia, acetoacetic acid, and formaldehyde gives the reaction. The chemical explanation of the reaction is still obscure. W. D. H.

The Relationship of the Thyroid Gland to the Physiological Action of Adrenaline. ERNST P. PICK and FRIEDRICH PINELES (*Biochem. Zeitsch.*, 1908, 12, 473—484).—The effect of adrenaline injection on the glycosuria and blood-pressure in thyroidectomised animals was investigated. It was found, in the case of rabbits, that the extirpation of the thyroid gland produced no effect on the action of adrenaline as regards its properties of producing glycosuria and diuresis, or of raising the blood-pressure. In the case of young goats, the removal of the thyroid, inhibited adrenaline-glyco-suria; the diuretic and blood-pressure-raising properties remained, however, intact.

S. B. S.

The Behaviour of Bromides in the Human and in Animal Organisms. II. H. von WYSS (*Arch. exp. Path. Pharm.*, 1908, 59, 186—195).—The kidneys possess no special capacity for elimination of bromides. After injection of these salts, owing to increased osmotic pressure, the kidneys will become active, but will eliminate, not the foreign salt necessarily, but also the chlorides. There will be,

consequently, a chlorine deficit in the organism, and the toxic effects due to bromides are caused by chlorine starvation; the bromides themselves play a purely passive rôle.

S. B. S.

Behaviour of Hydroxylamine in the Animal Organism. ROBERTO CIUSA and R. LUZZARTO (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 834—840).—The authors have made a number of experiments on the toxicity of hydroxylamine and on the presence of the latter or its oxidation products in the urine of animals to which hydroxylamine has been administered, either by ingestion or hypodermically; the blood of the animals was examined spectroscopically.

As a poison, hydroxylamine is four to five times as powerful as nitrous acid. In blood *in vitro*, hydroxylamine is oxidised, first to nitrous acid and then to nitric oxide, most probably with intermediate formation of dihydroxyammonia, thus: $\text{NH}_2\text{OH} \rightarrow \text{NH}(\text{OH})_2 \rightarrow \text{N}(\text{OH})_2$ or $\text{NH}_2\text{OH} \rightarrow \text{HNO} \rightarrow \text{HNO}_2$ and $\text{HNO} + \text{HNO}_2 = 2\text{NO} + \text{H}_2\text{O}$. The blood-spectrum indicates the presence of the nitric oxide compound of hemoglobin, together with methemoglobin. T. H. P.

Physiological Action of Optical Antipodes on Higher Organisms. GIUSEPPE BRUNI (*Gazzetta*, 1908, 38, ii, 1—5).—*l*- and *d*-Camphors were administered to a number of pairs of rabbits of about equal weight in the proportion of 1.5 gram of 10% camphor oil per 100 grams-weight of the animal, the times of survival of the rabbits after the injection being measured. In the case of *l*-camphor, the mean period of survival was 25.4 minutes, and for *d*-camphor, 336.7 minutes, so that the toxicity of *l*-camphor is thirteen times as great as that of the *d*-isomeride. Similar results were obtained by experiments on guinea-pigs. The tastes of the two forms of camphor are markedly different, the *l*-isomeride being almost tasteless.

T. H. P.

Behaviour of Dextrophenylosazone in the Organism. LUCIANO FIGORINI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 132—136).

Experiments on frogs, chickens, guinea-pigs, and dogs to which dextrophenylosazone was administered, either by ingestion or by subcutaneous or peritoneal injection, show that the animals are not affected by the osazone. The conclusion is drawn that the osazone is not resolved in the organism into dextrose and phenylhydrazine, or that, if such resolution does occur, phenylhydrazine is not set free; phenylhydrazine, when administered in the free state, reduces the oxyhemoglobin of the blood to methemoglobin, besides depressing the nerve centres.

T. H. P.

The Pharmacology of Phenanthrene and its Hydro-derivatives. HERMANN HILDEBRANDT (*Arch. exp. Path. Pharm.*, 1908, 59, 110—144).—The reduced phenanthrenes are less toxic than phenanthrene itself. The latter is eliminated from the organism in the form of a phenanthrol glyconate. Dodecahydrophenanthrene, in a rabbit, also gives rise to a glyconate. In the case of

frogs, phenanthrene itself gives rise to a glucuronate, but not 9:10-dihydrophenanthrene, or derivatives containing more hydrogen.

S. B. S.

The Quantitative Estimation of Synthetical Muscarine by Physiological Methods. HERMANN FÜHNER (*Arch. exp. Path. Pharm.*, 1908, 59, 179—185).—Injection of muscarine solutions into the heart of a toad (*Bufo vulgaris*) produces in weak solutions diminutions of amplitude of the beat; in stronger solutions, short cessation, with spontaneous recovery, with periodic beats, and with still stronger solutions, total cessation, lasting for some minutes. By perfusing the heart with Ringer's solution, it readily recovers, and can be employed for further experiments. To test the strength of a solution, the heart is first treated with known strengths of a muscarine solution, and the effects produced by each strength noticed. The heart is then perfused with the muscarine solution under investigation, and from the dilution necessary to produce the various effects, the concentration of the muscarine therein can be ascertained.

S. B. S.

The Action of Methyl-green. HERMANN FÜHNER (*Arch. exp. Path. Pharm.*, 1908, 59, 161—178).—Methyl-green is a true quaternary ammonium base, which cannot be extracted from aqueous solutions by ether. It has, accordingly, a curare-like action, and produces paralysis, acting peripherally. This effect is produced in frogs by doses of 2—4 milligrams. 0.03 Gram per kilo. is the toxic dose for rabbits when injected subcutaneously. Five times this dose, when administered *per os*, is without action. It exerts no muscarine-like action on the heart, but acts on the blood-vessels, causing fall of blood-pressure. Pharmacologically, it stands in the same relationship to the methyl-violet, from which it is produced by methylation, as curarine to curine; methyl-violet, like curine, exerts no curare-like action, but a digitalis-like action on the heart, which is wanting both in methyl-green and curarine. Methyl-violet is adsorbed by filter-paper and charcoal much more readily than methyl-green, and pigments strongly colour the tissues surrounding its point of application and the organs on which it exerts pharmacological action. Methyl-green, on the other hand, does not pigment very much, and is readily excreted by the kidneys. For this reason, the tinctorial power of methyl-green has failed to throw light on the question of the localisation of its curare-like action.

S. B. S.

The Pharmacology of the Quinotoxins. HERMANN HILDEBRANDT (*Arch. exp. Path. Pharm.*, 1908, 59, 127—139).—The products formed in the isomeric change produced by heating the cinchona alkaloids in acetic acid have been termed the quinotoxins. The experiments indicate that the increased toxicity of these products, as compared with the parent substances, is due to the presence of the piperidine group and the free imino-group. The comparative effects of cinchotoxin, methylcinchotoxin, and other derivatives were investigated.

S. B. S.

Biochemical Investigations of *p*-Iodophenylarsinic Acid. FERDINAND BLUMENTHAL and FRIEDRICH HERSCHMANN (*Biochem. Zeitsch.*, 1908, 12, 248—251).—*p*-Iodophenylarsinic acid was prepared from atoxyl by slowly diazotising it, and then adding potassium iodide. It is soluble in methyl and ethyl alcohols, but insoluble in other organic solvents, and can be heated to 300° without melting. For physiological investigations, the sodium salt was employed. It is more toxic than atoxyl; 0.1 gram can be injected into rabbits of from 1.5—2 kilograms in weight without marked ill-effects; 0.2 gram is a lethal dose. The animals killed exhibit acute nephritis. The iodine is excreted in the urine apparently in the form of an organic compound, and can be detected therein for some days after the injection. S. B. S.

Beeswax. RAGNAR BERG (*Chem. Zeit.*, 1908, 32, 777—780).—From a study of this wax, the author concludes that yellow beeswax contains aromatic and yellow colouring matters soluble in 80% alcohol and insoluble in light petroleum; chemically-bleached wax contains no such insoluble substances. The odour of the wax appears to be due, in part, to esters of a cholesterol derivative and acetic acid, butyric acid, valeric acid, and an unsaturated liquid acid. The operation of bleaching the wax causes the lower fatty acid esters to decompose. Both bleached and unbleached wax contain at least 0.6% (probably more) of cholesterol esters, which are difficult to saponify, and have high saponification values; only the alcohols give the cholesterol reaction, not the acids. The free wax acids, which are soluble in 80% alcohol, consist chiefly of unknown acids, together with small quantities of cerotic acid; the bleached wax contains palmitic acid. A supersaturation method is described for showing stearic acid adulteration of beeswax. Dilute acetone, D 0.8450, is used instead of alcohol, enabling so small a quantity as 0.3 gram of stearic acid to be detected in the presence of palmitic and cerotic acids. J. V. E.

Fatty Acids from Mummies. W. A. SCHMIDT (*Chem. Zeit.*, 1908, 32, 769—770). All mummies of whatever age contain fatty acids, and it is of interest to ascertain the alteration in composition of these acids as time progresses. With this object, mummies from about A.D. 500 and about A.D. 1000 have been investigated. From the lungs and muscles of the more recent, 60% and 20—25%, respectively of higher fatty acids have been obtained, 40% of which is oleic acid; practically no volatile fatty acids were present. The lungs and spleen of the older mummies contained respectively 12.5% and 30% of higher fatty acids, relatively less oleic acid, and in proportion to the more recent mummies, a considerable quantity of volatile acids.

The liver of a mummy (A.D. 1000) was found to contain 1.6% volatile fatty acids, which are, for the most part, present as the sodium salt.

The author considers that the presence of higher acids is probably due, in part, to the transformation of the mummified albumin, and that the volatile acids may be derived from the slow decomposition of the higher acids, and not directly from the albumin. J. V. E.

Optical Activity of "Protagon." A New Physical Phenomenon Observed in Connexion with the Optical Activity of So-called "Protagon." ORTO ROSENHEIM and M. CHRISTINE TEBB (*J. Physiol.*, 1908, 37, 341—347, 348—354).—"Protagon" dissolved in pyridine possesses at 30° a slight dextrorotatory power, which changes to optical inactivity at higher or lower temperatures, showing finally a maximum levorotation of -242° , and a final constant levorotation of $[\alpha]_D^{20} -13.3^\circ$. The prolonged action of boiling or warm alcohol during its preparation or recrystallisation has no influence on these phenomena. Wilson and Cramer's "decomposition" theory of protagon, based on the change of the specific rotation of protagon in pyridine from $+6.8^\circ$ to $(+1)13.3^\circ$ after the action of warm alcohol, is erroneous, and cannot be used for the revival of the view that protagon is a definite chemical compound.

The explanation of the change is as follows: the diamino-phosphatide, sphingomyelin (the constituent of "protagon" rich in phosphorus), is precipitated, when a solution of protagon is kept; it is the appearance of this precipitate which gives rise to the high levorotation; as the precipitate settles, the levorotation decreases, and the final levorotation is due to a small amount of the precipitate which does not settle. But if the precipitate is removed by filtration or centrifugation, the portion of the protagon which remains in the pyridine solution, and is phosphorus-free, is optically inactive. If the precipitate is once more shaken up with this, high levorotation is again obtained, which lessens as the precipitate once more settles. The high levorotation is expressed in the usual way, but the optical activity of the precipitated substance does not follow Biot's laws.

On microscopic examination, the precipitate of sphingomyelin is found to consist of anisotropic globules (fluid spherocrystals), and their appearance in polarised light is figured. The term *sphaerorotation* is proposed for this phenomenon.

The majority of the experiments recorded were performed with protagon or sphingomyelin prepared from brain, but a similar substance with the same remarkable properties was also prepared from the cortex of the suprarenal body.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Enzymos [Diastase]. WILHELM SCHNEIDEWIND, DIEDRICH MEYER, and F. MENTER (*Bied. Zentr.*, 1908, 37, 503—504; from *Arb. Agric.-hem. Versuchstat. Halle*, 1906, 2, 67).—Alcohol and ether have a very injurious effect on the action of diastase, and freshly-prepared solutions of diastase are much more vigorous in action than the precipitated substance. It is therefore impossible to obtain information as to the composition of enzymes by studying substances prepared by precipitation.

Albumin, asparagine, and peptone act favourably, so also do weak acids (citric and acetic) at low concentrations (0.001%), but at higher concentrations (0.010%) they retard the action of diastase. Chlorides of the alkalis and small quantities of monophosphates and of aluminium sulphate accelerate the action. One to 2% of monocalcium phosphate or of aluminium phosphate inhibits action altogether. E. J. R.

Action of Small Quantities of Metals on Lactic Acid Fermentation. CHARLES RICHER (*Biol. Zentr.*, 1908, 37, 576; from *Compt. rend. Soc. Biol.*, 1905, 60, 455—456).—Minute amounts of barium, platinum, cobalt, manganese, and vanadium were found to cause a slight acceleration in the rate of production of lactic acid.

E. J. R.

The Catalases of Bacteria. AUGUST JORNS (*Arch. Hygiene*, 1908, 67, 134—162).—The power of bacteria in bouillon cultures to decompose hydrogen peroxide is due to the presence of a specific catalase, which exists in the form of both an ecto- and endo-ferment. Catalase-formation appears to be a very general property of bacteria, although individual species vary very greatly as regards the intensity of the action. S. B. S.

The Chemical Changes Involved in the Assimilation of Free Nitrogen by Azotobacter and Radiobacter. JULIUS STOKLASA (*Zentr. Bakt. Par.*, 1908, ii, 21, 484—509).—Both *Azotobacter chroococcum* and *Radiobacter* are widely distributed in nature, especially in soils where the bluish-green algae are numerous; they were not found, however, in the high-lying soils of the Alps. Full details are given of the methods of isolating and studying the organisms.

Experiments on the amount of nitrogen-fixation showed that, contrary to the generally-accepted view, *Radiobacter* has only slight powers of assimilating free nitrogen; thus cultures in 10 and 20 days respectively fixed only 2.2 and 5 milligrams of nitrogen per litre, whilst *Azotobacter* cultures under the same conditions fixed 74.9 and 98 milligrams per litre. Nor is the nitrogen-fixing power of *Azotobacter* greatly increased by symbiosis with *Radiobacter*.

In order that nitrogen-fixation should go on, it is essential that carbohydrate should be supplied, and experiments were made to ascertain the relative values of several sugars. *L*-Arabinose was the most effective, causing 180 milligrams of nitrogen per litre to be fixed; under the same condition, *L*-xylose, dextrose, *D*-galactose, and levulose enabled 140 to 155 milligrams to be fixed, sucrose 125, maltose 86, but rhamnose only 19.8. The figures for duplicate experiments show somewhat wide variations, but a series of tests with dextrose showed that 99 to 224 grains of this sugar were converted into carbon dioxide and water for every gram of nitrogen fixed. In view of the above results, the author suggests that the furfuroids of the soil furnish the best source of food for *Azotobacter*.

The influence of sodium nitrate on the process was also investigated. This substance inhibits nitrogen-fixation; nevertheless, it is not nearly as useful a food stuff as free nitrogen. *Radiobacter* is a power-

ful denitrifier, decomposing the nitrate with liberation of free nitrogen.

Respiration is more intense than in any other organism yet studied, 1 gram of the bacterial mass evolving 1.3 grams of carbon dioxide in twenty-four hours. In addition to carbon dioxide, the following substances are also produced from the sugar: ethyl alcohol, hydrogen, formic, acetic, butyric, and lactic acids.

E. J. R.

Effect of Pasteurisation on the Development of Ammonia in Milk. W. G. WHITMAN and HENRY C. SHERMAN (*J. Amer. Chem. Soc.*, 1908, 30, 1288—1295).—Experiments which have been made on the pasteurisation of milk at 65° and 85° have shown that it does not entirely destroy the bacteria which attack the proteins with formation of ammonia, but does destroy, sometimes at 65° and always at 85°, the bacteria or enzymes which cause the decrease of ammonia in raw milk. The estimation of ammonia for the purpose of determining the amount of decomposition of proteins in milk is particularly useful in samples which have been pasteurised at a high temperature, but is of less value in samples which have been pasteurised at low temperatures or not at all, since the amount of ammonia present at any given time cannot be assumed to be proportional to the extent to which protein decomposition has taken place. In the case of samples of New York milk, it was found that, in general, pasteurisation was less efficient in checking the development of ammonia than in retarding the production of acid, and this was especially true of milk pasteurised at the higher temperature (85°), which before becoming sour often showed an amount of ammonia considerably in excess of that produced in raw milk of the same age and origin. It was also found that pasteurisation greatly retarded souring, but favoured the development of an offensive odour and bitter taste, this effect being much less noticeable in samples pasteurised at 65° than in those pasteurised at 85°.

E. G.

The Photodynamic Action of Plant Extracts Containing Chlorophyll. WALTHER HAUSMANN (*Biochem. Zeitsch.*, 1907, 12, 331—334).—Extracts of various plants containing chlorophyll were shown to exert no hemolytic action on suspensions of red blood-corpuscles when kept in the dark; if the mixture of corresponding quantities was exposed to light, hemolysis readily took place.

S. B. S.

Recent Researches on Chlorophyllian Photosynthesis. EVA MANELLI and GINO POLLACCI (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 739—744).—A destructive criticism of the work of Usher and Priestley (*At. tr.*, 1906, ii, 299, 881; compare also Ewart, this vol. ii, 217). The statement made by Usher and Priestley that green leaves of *Elodea*, still attached to the plant, do not become reddish-violet when immersed in Schiff's reagent is incorrect. Moreover, when *Elodea*, killed by immersion in boiling water, is placed in pure water, the same bleaching is seen as was observed by Usher and Priestley in a solution of carbon dioxide; it is probably due to the action of oxygen on the chlorophyll, and not to that of carbon dioxide. The experiments on the production of formaldehyde from carbon

dioxide in an artificial "cell" composed of glycerol and chlorophyll are valueless, because solutions of chlorophyll always give Schiff's reaction. The evolution of oxygen from these artificial cells, as described by Usher and Priestley could not be observed. In conclusion, it is pointed out (1) that these workers did not make any direct experiment to prove the presence of hydrogen peroxide in plants; (2) the function of the catalytic enzymes supposed to decompose the hydrogen peroxide is not demonstrated; (3) that all deductions based on the existence of formaldehyde in the plant after the death of the protoplasm and the bleaching of the chlorophyll are erroneous, because formaldehyde is present in the living green cells; (4) that the photolytic decomposition of carbon dioxide in presence of chlorophyll cannot be realised, much less the production of starch under the conditions given by Usher and Priestley. The only facts established are that the phenomena of assimilation are intimately connected with the production of formaldehyde, and that the latter is localised in the chloroplastids, as was already observed by Kimpflin. W. A. D.

The Translocation of Nitrogen Compounds into the Embryo of Barley from the Endosperm and from Artificial Culture Solutions. HORACE T. BROWN (*Trans. Guinness Lab.*, 1, 11, 288. Compare following abstract).—Germinating barley has been shown to contain in the early stages of its life a variety of nitrogenous substances arising from the protein of the original seed; within the first ten days, at least 35% of the seed protein must be transformed. Not all of the nitrogen compounds found after germination are degradation ("down-grade") products; a certain amount represents the surplus nitrogen over and above that required for immediate tissue formation in the growing embryo, and temporarily accumulated for future use ("up-grade" products). It would be possible to discriminate between the two by stopping the vital activity of the embryo in germinating grain without stopping enzyme action, for example, by treatment with chloroform vapour. Useful light is also thrown on the subject by determining the relative nutrient value of the various nitrogenous constituents of the growing grain when these are presented to the detached embryo in water cultures (compare Brown and Morris, *Trans.*, 1899, 57, 483).

The barley was softened somewhat by steeping, and the embryo removed without injury by means of a small knife. A certain number of the embryos were then placed, scutellum downwards, on disks of porous porcelain immersed in Petri dishes containing the nutrient solution in such quantity that the disk was covered without drowning the embryos. The amounts of mineral matter and of sugar supplied were the same in all experiments, but the nitrogen compounds were varied. The compounds used, and the order of their effectiveness, are as follows: tyrosine and phenylalanine (both poisonous at the concentration used); leucine, malt albumoses, and malt peptones (tend to inhibit growth of the plantlets); choline, betaine, allantoin (directly effective as nutrients, and causing assimilation of nitrogen amounting to nearly 50% of that originally present); ammonium sulphate,

aspartic acid, glutamic acid, potassium nitrate, and asparagine show progressive increases in their power to supply nitrogen to the plant.

It is significant that asparagine, the best nutrient found, is much more effective than its hydrolytic products, just as sucrose was found by Brown and Morris to be superior as a nutrient to dextrose and levulose.

E. J. R.

The Soluble and Non-coagulable Nitrogen Compounds in Malt. HORACE T. BROWN (*J. Inst. Brewing*, 1907, 13, 394—416).—An aqueous extract of malt contains a very complex mixture of nitrogenous substances, even after boiling and removal of the coagulated compounds, and ordinary precipitants were found insufficient to effect complete separations. Thus phosphotungstic acid precipitates about half the nitrogen, but it does not sharply differentiate the complex compounds, and it is possible to isolate both from the precipitate and the filtrate substances having substantially the same properties. Special methods were devised for estimating the nitrogen present as ammonia, and that existing as amides and amino-acids (and therefore liberated by nitrous acid), but these only accounted for 12.5% of the total nitrogen in the extract. An elaborate series of experiments was then made to separate and characterise the remainder of the nitrogen compounds, including salting-out with zinc sulphate and ammonium sulphate, various treatments with alcohol, precipitation with phosphotungstic acid, and the use of dialysis in a special form of dialyser; as far as possible, the experiments were made quantitatively. In this way, some substances were isolated re-sembling in their main characteristics the albumoses and peptones which result from the digestion of animal proteins under the influence of animal pepsins. The malt albumoses are neutral, soluble in water, not coagulated by heat, and salted-out by ammonium and zinc sulphates. The malt peptones are readily and permanently soluble in water and strong alcohol, are readily diffusible, and precipitable by phosphotungstic acid. In all these respects they agree with the corresponding animal products; they differ, however, in not giving the biuret reaction, and in that the malt peptones are not precipitable by ferric ammonium alum. The 'division of the "non coagulable" nitrogen in aqueous and dilute alcohol extracts of malt was found to be as follows:

	Aqueous extract of malt.	Dilute alcohol extract of malt.
Nitrogen as ammonia	3.5	2.0
" " amino-acid and amide	8.5	16.0
" " organic bases	4.0	8.0
" " malt albumoses	20.0	16.0
" " malt peptones	31.0	38.0
" " undetermined substances ..	33.0	—
	<hr/> 100.0	<hr/> 100.0

The amino-acids and amides include asparagine, tyrosine, leucine, and allantoin; the organic bases are mainly betaine and choline; the albumoses consist of at least three distinct compounds, and the peptones can be differentiated into at least two.

In examining the several fractions obtained during the investigation of the albumoses and peptones, the author has found the "amino-index" a useful factor. These substances, although neither amino nor amino-acids, liberate a certain amount of their nitrogen on treatment with nitrous acid, and the percentage so liberated is called the amino-index.

Malt albumose I, which represents about one-third of the albumoses separable by ammonium sulphate, is insoluble in 80% alcohol, and possesses a remarkable power of producing a persistent froth in aqueous solution, a property of considerable interest in connection with the formation of "head" or foam on malt-worts and beer; its amino-index is 4. Albumose II is soluble in 85% alcohol, and does not possess this frothing power; its amino-index is 5. Albumose I with amino-index 20, is salted-out with zinc sulphate after removal of Albumoses I and II.

The malt peptones I and II closely resemble each other in general properties, but the amino-index of one is 10.9, and of the other, 19.2.

The author considers that the albumoses and peptones are derived from hordein, the alcohol-soluble protein of barley. E. J. R.

The Protein Changes Taking Place in Green Plants when Kept in the Dark. W. BERKEWITSCH (*Biochem. Zeitsch.*, 1908, 314—330).—The plants employed in the investigations were beans and oats. The total nitrogen was estimated by Kjeldahl's method, the protein nitrogen by that of Stutzer, the aspartic nitrogen by that of Sachsse, and the ammonia nitrogen by the Boscward. In the case of beans, the undigestible nitrogen and the nitrogen of the substances precipitable by phosphotungstic acid were also estimated. The analyses were carried out with samples of the original material, and also with samples of material which had remained for different lengths of time in the dark. It was found that there was a decrease of protein nitrogen and an increase of aspartic acid nitrogen. The nitrogen, which was due neither to aspartic acid nor protein, at first increased, and then diminished. The conclusion is drawn that part of the aspartic acid (and another accompanying amide) is formed by a secondary change from products of protein degradation, which include leucine and tyrosine. S. B. S.

The Function of Calcium in Plants. VIKTOR GRAFE and LEONOLD RITTER von PORTHEIM (*Biol. Zeitsch.*, 1908, 37, 571—577 from *Naturw. Rundschau*, 1907, 22, 255).—The authors find that the injurious effects observed when plants are grown without a proper supply of calcium compounds either fail to appear or are greatly delayed when sugar is supplied. The experiments were made with beans (*Phaseolus vulgaris*), and the sugars investigated were levulose, dextrose, and sucrose; of these, levulose was most effective in delaying the effects of calcium starvation. These results support the view that calcium is concerned in the conversion of starch into sugar in the plant.

Experiments were also designed to ascertain whether calcium acts as a protector against the formaldehyde, which may be supposed

produced during the assimilation of carbon dioxide. Plants were grown in normal solutions and in solutions free from calcium; some were kept in the dark and some in the light. Formaldehyde occurred in all plants exposed to light, but it did not occur in plants kept in the dark, even where calcium was withheld. Nevertheless, the characteristic effects of calcium starvation were seen in the latter case, and these experiments do not show any relation between calcium starvation and presence of formaldehyde. E. J. R.

Occurrence of Calcium Oxalate in the Barks of the Eucalyptus. HENRY G. SMITH (*J. Roy. Soc. New South Wales*, 1905, 39, 23—32).—The following amounts of calcium oxalate were found in the bark of different species of *Eucalyptus*: *E. acilis*, 16.66; *E. Behriana*, 16.50; *E. salubris*, 16.00; *E. oleosa*, 16.4; *E. dumosa*, 9.80; *E. salmonophloia*, 8.34; *E. occidentalis*, 8.2; *E. viridis*, 5.01; *E. redunca*, 4.46; *E. polybractea*, 2.14; *E. stricta*, 0.69, and *E. Morrisi*, 0.08%. The calcium oxalate differs from that usually found in plants in having only one mol. H_2O , and its crystalline form, being similar to the mineral whewellite.

It is suggested that the production of large amounts of oxalic acid may be the cause of stunted growth, and that *Eucalyptus gracilis* is the degenerate form of a larger tree.

The tannin in the barks containing much calcium oxalate is decidedly superior to the tannin of barks in which only small amounts are present. N. H. J. M.

Aluminium, the Chief Inorganic Element in a Proteaceous Tree, and the Occurrence of Aluminium Succinate in Trees of this Species. HENRY G. SMITH (*J. Roy. Soc. New South Wales*, 1904, 37, 107—120).—Four specimens of *Writes excelsa*, one of the trees known in Australia as "Silky Oak," were found to contain large amounts of aluminium. When excessive amounts of aluminium are taken up by the trees, deposits of basic aluminium succinate are formed. The deposits contain also free butyric acid.

Samples of the wood from (1) Queensland, (2) Mullimbimby, (3) Dorrigo, and (4) Bangalow, contained 0.639, 0.684, 0.673, and 706% ash, the composition of which was as follows:

	K ₂ O	Na ₂ O	CaO	MgO	Al ₂ O ₃	Mn ₂ O ₃	P ₂ O ₅	SO ₂	SiO ₂	Cl	CO ₂
1.	6.98	trace	1.99	3.59	79.61	0.36	0.36	0.15	3.64	0.25	2.54
2.	10.91	1.59	11.25	13.87	36.01	3.01	1.31	0.13	0.62	3.03	18.82
3.	14.96	1.13	2.63	16.12	43.03	trace	1.70	0.26	0.36	1.54	(18.62)
4.	—	—	—	—	38.77	0.18	1.26	—	—	—	—

The ash of (2) contained traces of cobalt. Iron was present only in traces.

The sap of *Grevillea robusta* was found to contain butyric acid. No aluminium could be detected in the ash of five varieties of *Grevillea*.

N. H. J. M.

Chocor Fat. JULIUS LEWKOWITSCH (*Analyst*, 1908, 33, 313—315).—A fat, consisting of about 98% of myristin and 2% of capric acid, is yielded by the seeds of *Scyphocephalum ochocoa*, a tree

found on the West Coast of Africa. The kernels of the seeds yield about 58.8% of the fat, but by whatever process the fat is prepared a dark brown colouring matter is at the same time extracted; this colouring matter is contained, not only in the husks, but also in the spermoderm which passes through the whole of the endosperm in form of irregular lamellæ. The white endosperm, cut out carefully by hand, yielded a fat having the following chemical and physical constants: D₄ 0.8899; saponification number, 238.5; iodine number, 172; Reichert-Meissl number, 0.65; m. p. 45—48°; unsaponifiable matter, 0.37%; mean molecular weight of the fatty acids, freed from unsaponifiable matter, 221.9; m. p. of fatty acids, 47.2°; the extra fat had the acid number 1.42. The seeds are obtainable in large quantity.

W. P.

Carotene from Carrots. LEON MARCHLEWSKI (*Zeitsch. phys. Chem.*, 1908, 53, 554. Compare Euler and Nordenson, this vol. 724).—The author has shown previously that carotene when oxidised does not yield a derivative of cholesterol.

J. J.

Absence of Gum and Presence of a New Diglucoside in Kinos of the Eucalyptus. HENRY G. SMITH (*J. Roy. Soc. New South Wales*, 1905, 38, 21—36).—Freshly-exuded kinos of *Eucalyptus paniculata* yielded a diglucoside, *emphloin*, which is insoluble in alcohol. When hydrolysed, it yields 44.47% of a sugar, from which an *osazone* m. p. 176—178°, was obtained. The sugar, which is probably isomeric with melibiose, is without optical activity, presumably owing to internal compensation.

When the glucoside is boiled with dilute acid, a precipitate of "red" is produced. This yields protocatechuic acid when heated with potassium hydroxide.

The astringency values of about 160 species of *Eucalyptus* were determined. Compared with gallic acid, containing 11.43% water, ~1000, the values for *E. pilularis*, *E. macrorrhynchos*, *E. eugeninoides* (containing about 18% of water) were 838, 835, and respectively. The kinos of *E. paniculata* and other "iron-barks" are only about half their values, owing to their glucosidal nature, and it will be necessary to hydrolyse the glucoside while in the pits (perhaps by means of an enzyme) to render them suitable as tanning material.

N. H. J.

Barks of Rhamnus Frangula and Rhamnus Purshii. ALEXANDER TSCHURCH and J. F. A. POOL (*Arch. Pharm.*, 1907, 243, 315—325).—The emodins isolated from the two barks are identical: a substance, m. p. 165°, which was, in addition, obtained from *Frangula* bark, is probably chrysophanic acid; neither bark contains it. Tschurch and Edner's assay method for rhabarbar (At. 1907, ii, 515) is not applicable to the barks in question, but Wainman's colorimetric method (Abstr., 1905, ii, 659) appears to be of great importance. The addition of magnesia to the powdered drug before percolation, in order to remove the bitter taste from the extract, does not greatly affect the total hydroxymethylanthraquinone content of

colate, but increases in it the amount of combined hydroxymethyl-sinraquinones.
G. B.

Origin of the Colour of Red Grapes. PHILIPPE MALVEZIN *apl. rend.*, 1908, 147, 384—386.* Compare Laborde, this vol., ii, 11.—When unripe, green berries of red grapes are heated with tilted water for seventeen hours at 85°, an intense yellow colour developed, which at the end of twenty-four hours changes to red. The red coloration is due to oxidation by the air, since in absence of air only the yellow colour is obtained. A similar series of colour changes occurs when green berries of white grapes are treated in the same way. The leaves and stalks of the vine, however, give only the same colour.

The author ascribes the red colour of grapes to the existence of a latent chromogenic compound, which in his experiments is transformed to the red substance under the influence of air, heat, and probably also the same transformation being brought about in nature by a specific enzyme. The absence of colour in white grapes is considered to be due to the absence of this enzyme. The chromogenic substance is unstable, and is precipitated when the heating at 85° is prolonged; raising the temperature, however, the original brilliant red colour appears, and this process can be repeated a certain number of times.

W. O. W.

The Action of Sulphur Dioxide on Plants. A. WIELER (*Bied. tr.*, 1908, 37, 572—573; from *Naturw. Rundschau*, 1907, 22, 229). Assimilation of carbon dioxide is profoundly influenced by the presence of sulphur dioxide, but respiration is not affected. Examination of the leaves of plants from districts where sulphur dioxide injury showed that this substance is present in the leaf, though only in small quantities, except in cases where the leaves are close to the source of origin of the gas, when larger amounts are found. Sulphur dioxide enters through the stomata, and causes greater injury in wet than in dry weather, because the stomata are more easily open. There is evidence that some other factors come into play besides the action of sulphur dioxide in the leaf; for instance, the soils in districts where injury arises are acid. It is concluded that injury usually can be overcome by suitable manuring, and, in particular, by liming.
E. J. R.

The Quantity of Arsenic contained in Wines obtained from vines which have been Treated with Arsenical Washes. G. BRETEAU (*J. Pharm. Chim.*, 1908, [vi], 23, 154—158).—Ten samples of wine obtained from vines which had been treated with arsenical washes or sprays were found to contain quantities of arsenic varying from 0.003 to 0.20 milligram per litre; one sample was free from arsenic. Four other samples, also coming from vines similarly treated, but which had received the addition of quantities of sulphuric acid, bisulphite, &c., contained from 0.03 to 0.10 milligram of arsenic per litre.
W. P. S.

* And *Bull. Assoc. chim. Sac. Dist.*, 1908, 26, 187—189.

Tobacco-smoke. JOSEF HABERMANN and RICHARD EHRENFELD (*Zeitsch. physiol. Chem.*, 1908, 58, 363—372. Compare Abstr., 1908, ii, 680).—An investigation of the amount of ammonia, sulphur, nicotine in the smoke of various brands of Austrian cigars.

W. D. 1

Composition of the Air in Soils. ERICH LAU (*Bied. Zeitsch.*, 1908, 37, 433—434).—The author discusses the variations in amount of carbon dioxide present in the air of the soil. The soil is richest in carbon dioxide in summer and poorest in winter, maximum being reached in July, and the minimum in February. Small amounts are found in sandy soils, more in clays and loams, a still larger quantity in peaty soils, corresponding with the increased amounts of humus present; the physical properties of the soil influence the quantity. Less is found at the surface than lower down; the difference is more marked in the case of peaty than of sandy soils. The amount of oxygen in the soil air depends on the amount of carbon dioxide, hence it is clear that the latter is formed by oxidation of humus.

Some of the carbon dioxide is also produced by the plants growing in the soil, and the amount present in soils carrying crops is also greater than in fallow soils; the amount also increases with temperature and the weight of the crop. Potatoes and lupines especially cause an increase in the carbon dioxide, indicating that their respiratory processes are more intense than those of other plants.

Dung also increases the amount of carbon dioxide present.

E. J.

Some Properties of the Organic Matter in the Soil. Osmotic Pressure of the Soil Moisture. JOSEF KÖNIG, JOHANN HASENBAUMER, and H. GROSSMANN (*Landw. Versuchs.-stat.*, 1907, 69, 1—92).—The authors have examined a method suggested by Copenrath (*Landw. Versuchs.-stat.*, 1907, 66, 401) for determining the amount of available plant food in soils, namely, heating the soil (500 grams) with water (5 litres) for five hours under 5 atm. pressure. The plant food goes into solution either as complex salts or as organic substances. Great differences in composition, such as would be found in soils of widely different types, are thus brought out, but no slight differences produced by adding to a given soil artificial manure in quantities commensurate with those used in practice. Hydrogen peroxide also dissolves plant food from the soil, and in some cases higher quantities than the above method, but it also fails to discriminate between manured and unmanured soils of the same type when the amount of added manure is only small.

The analytical value of the method was established by pot experiments, which showed that the amount of potash taken by the plants and therefore "available" for the plant, was much the same as that dissolved by the above processes. Since the amount of plant food dissolved by these methods is higher than that extracted by pure water or water saturated with carbon dioxide, it follows that some of the soil humus must furnish mineral matter to the plant. For the

on, potash appears to be set free from some of its insoluble compounds during the growth of the plant.

An apparatus is described by means of which a measure of the osmotic pressure of the soil solution can be obtained. It is suggested that such measurements might throw much light on the solubility of soil constituents.

E. J. R.

Isolation of Picolinecarboxylic Acid from Soils and its Action on Soil Fertility. OSWALD SCHREINER and EDMUND C. REED (*J. Amer. Chem. Soc.*, 1908, 30, 1293--1307).—A sample of soil from Takoma Park, Md., was found to contain 3% of organic matter, 0.1% of nitrogen, and sufficient mineral substances for many crops. Nevertheless, this soil was very unfertile, and did not respond readily to treatment with manures. It was found that this was due to the presence of toxic substances, and a careful investigation was therefore carried out, with the result that picolinecarboxylic acid was isolated.

Picoline-4-carboxylic acid was obtained by Böttger (Abstr., 1881, 1884, 758) by the action of heat on uvitonic acid, the latter being easily prepared by treating pyruvic acid with alcoholic ammonia. No evidence was obtained of the presence of pyruvic acid in the soil, and no evidence could be obtained of the presence of uvitonic acid.

A series of experiments has been carried out with a view to ascertaining the toxicity of various organic substances on wheat and beans (compare Schreiner and Reed, this vol., ii, 426). It has been found that picolinecarboxylic acid in very low concentrations acts as a stimulant, but is decidedly injurious when present to the extent of 100–200 parts per million. The amount of picolinecarboxylic acid in the Takoma Park soil was not sufficient to account for the full effect, but this was chiefly due to the presence of dihydroxy-pyruvic acid. Uvitonic acid is much more toxic than picolinecarboxylic acid.

Pyruvic acid exerts a toxic action, but its sodium salt is not so. Pyridine and picoline are very injurious, and piperidine is more so.

E. G.

Effect of Lime on the Availability of the Soil Constituents.

ERICK B. GUTHRIE and L. COHEN (*J. Roy. Soc. New South Wales*, 1907, 41, 61--66).—About 10 lb. of a light sandy soil, a heavy loam fairly rich in humus, and a very stiff clay were mixed with 1% freshly-slacked lime and, along with duplicate portions of each, out-lime, exposed to the sun and rain for a month, being kept in the whole time.

The clay to which lime was added became friable in a fortnight. In soils which had no lime, the water-soluble phosphoric acid decreased considerably, and in the case of the clay soil the water-soluble potassium was also reduced as well. Application of lime lessened the decrease in water-soluble constituents, and in the sandy soil increased the proportions of phosphoric acid and potassium soluble in water above those naturally present.

The amounts of constituents soluble in citric acid changed very little, and the effect of liming was less marked.

As regards the soluble nitrogen, application of lime was found to increase the amount of nitrites, whilst the amount of nitrates remained almost the same, except in the case of the clay soil, which showed a loss of nitrate under the influence of lime. The largest amount of soluble nitrogen in the unlined soil was in the form of ammonia, of which the lined soil contained very little.

N. H. J. :

Chemical Examination and Calorimetric Test of Indiana Peats. R. E. LYONS and C. C. CARPENTER (*J. Amer. Chem. Soc.*, 1908, 30, 1307—1311).—Twenty-nine samples of peat from the region of Northern Indiana have been tested for calorific value; five typical specimens of Indiana peats have been submitted for complete analysis. The maximum heating effect was given by a specimen of sphagnum moss peat from a bed 20 feet thick exhibiting almost complete decomposition and a dark chocolate color, whilst the minimum effect was given by an immature, highly oxidized peat derived from grass and sedge. In general, the results show that the best Indiana peat has a calorific value equal to the best grade of peat found in other parts of the United States and in Europe.

E.

Manurial Trials with Calcium Cyanamide and (Sweet) Calcium Nitrate. HJALMAR VON FEILITZEN (*Biol. Zentr.*, 1908, 498—499; from *Landwirtsch. Presse*, 1907, 229 and 243; see Abstr., 1906, ii, 487).—The experiments show that calcium cyanamide acts almost as favourably as ammonium salts, although not as well as sodium nitrate, on oats, barley, wheat, and potatoes growing on sand or clay soils. It also acts well on the better moor soils (Misch-Niederungsmooren), but on the poorer soils (sphagnum and heath moorland) it was not as good.

Calcium nitrate gave much better results, and was fully as good as sodium nitrate even on the high moorland soils; indeed, on oats it was better than sodium nitrate.

E. J.

Pot Experiments to Determine the Limits of Endurance of Different Farm Crops for Certain Injurious Substances. FREDERICK B. GUTHRIE and R. HELMS (*J. Roy. Soc. New South Wales*, 1904, 37, 165—171. Compare Abstr., 1905, ii, 753).—The following numbers indicate the percentages of the different substances employed and their effect on maize grown in a fairly rich garden loam.

	NaCl	Na ₂ CO ₃	NH ₄ CNS.	Na ₂ SO ₄	As
Germination affected ..	0.29	0.29	0.005	0.001	—
“ prevented ..	0.50	0.50	above 0.02	above 0.006	above 1
Growth affected ..	0.16	0.10	0.001	0.001	—
“ prevented ..	0.25	0.25	above 0.02	0.004	—

N. H. J.

Amount and Composition of Drainage Waters collected during the Year 1906-7. J. M. HAYMAN (*Rep. Ceylon Agric. Dept.* for the year ending June 30, 1907, 57—58. Compare Abstr., 1907, ii, 127).—Results of analyses, made twice a month, of the drainage

ough four drain-gauges, two 72 inches and two 36 inches deep, from April to October 31.

The total amounts of rain and drainage, and of nitrogen as nitrates and drainage, for the five months were as follows:

No.	Depth of soil, in inches.	Rainfall, in inches.	Drainage, in inches.	Nitrogen	
				Per million.	Lb. per acre.
.....	72	34.38	19.126	41.66	180.31
.....	72	34.38	16.709	53.03	200.51
.....	36	34.38	18.257	14.79	60.75
.....	36	34.38	19.052	15.99	85.62

N. H. J. M.

Analytical Chemistry.

Importance of Hygroscopy in General Analysis. C. L. F. YARD (*Pharm. Zentr.h.*, 1908, 49, 759—763). Attention is called to the deductions which may be drawn as to the nature of a compound from an observation of its hygroscopic properties. Instances are given of salts which are similar in appearance, but may be distinguished from one another by one having the power of absorbing water from the atmosphere. Thus, a crystal of sodium iodide, exposed side by side with a crystal of potassium iodide, will absorb enough water to give a complete solution, whilst the potassium salt remains practically dry. Barium chloride is readily distinguished from the hygroscopic calcium and strontium chlorides. Sodium metaphosphate is hygroscopic, and differs from sodium orthophosphate in this respect. Salts exhibiting this difference are potassium acetate and sodium acetate, copper sulphate and copper nitrate, &c.

W. P. S.

Qualitative Centrifugal Analysis. B. C. P. JANSSEN (*Chem. Ind.*, 1908, 5, 591—593). The author finds that the use of the centrifuge in qualitative analysis affords a method which is superior to the ordinary filtration process in speed, ease of manipulation, and cleanliness. Its use is not more expensive than that of good filter paper.

A. J. W.

Qualitative Analysis. J. P. WHITE (*Chem. Weekl.*, 1908, 5, 623—625). Theoretical paper, criticising Anema and van Deventer's conclusions (this vol., ii, 221).

A. J. W.

Compound Gas Pipette. HANS FLEISSNER (*Chem. Zeit.*, 1908, 32, 100). The troublesome operation of filling the compound Hempel pipette is avoided by having a small vertical tube sealed to the connection tube of the central top bulb. When the pipette is filled with the aid of a funnel and a piece of rubber tubing, the tube is closed with a rubber tube carrying a glass rod.

L. J. K.

Physico-chemical Analysis of Wines. PAUL DUTOIT MARCEL DUBOIX (*Compt. rend.*, 1908, 147, 351—353. Compare vol. ii, 781).—Berthelot's method for determining the end point in acidimetry by means of the electrical conductivity of the solution furnishes higher results when applied to the analysis of the distillates of wines than the usual process. The total quantity of volatile substances exceeds the amount of ammonia determined gravimetrically or colorimetrically; the difference represents the volatile organic bases, the quantity of which varies considerably with the nature and age of the wine. The method has also been employed to estimate the volatile acids, but the results are found to depend to a certain extent on the method of carrying out the distillation.

Estimations of the organic bases and colloidal tannins have shown a deficiency of one or both of these constituents in inferior wines ("piquettes") and wines prepared from raisins. W. O. W.

Qualitative and Quantitative Separation of Metals. EMMANUEL POZZI-ESCOFFIER (*Bull. Soc. chim. Belg.*, 1908, 22, 327—333). A new course shown in six tables and including the rarer metals. The process much resembles the ordinary course, but deviates from this in the treatment of the filtrate resulting from the action of hydrogen sulphide. This, after expelling the hydrogen sulphide by boiling, is mixed with an excess of sodium hydrophosphate, sodium hydroxide, and sodium hypobromite, and is boiled. L. DE

Detection and Estimation of Free Mineral Acids in Wines. CHARLES ASTRE (*Bull. Soc. chim.*, 1908, [iv], 3, 928).—The process depends on the partial separation of the mineral acid from the other constituents of the wine by dialysis. For quantitative purposes, parallel experiments are made with the suspected wine and one of similar type, the dialysed products being titrated with alkali. Details as to the quantities to be used, &c., are given in the original. T. A.

Simple Method for the Estimation of the Halogens in Mercuric Chloride and Mercuric Bromide. MORITZ (*Zeitsch. anorg. Chem.*, 1908, 59, 271—272).—Mercuric chloride and mercuric bromide are decomposed by alkaline solutions of hydrogen peroxide more readily than the iodide (compare this vol. ii, 696). Mercuric mercury separates, and is filtered off after the solution has been heated to near its boiling point to remove the excess of hydrogen peroxide. The halogen in the solution is then estimated by means of sodium nitrate. H. M.

Rapid Estimation of Sulphur in Coals. ABRAHAM KOMAROW (*Chem. Zeit.*, 1908, 32, 770).—A combination of Brunck's process of combustion with cobaltic oxide and sodium carbonate in a current of oxygen (*Abstr.*, 1905, ii, 762) and the author's barium chromate method (*Abstr.*, 1907, ii, 577). L. DE

estimation of Sulphur in Mineral Sulphides. V. HASSREIDTER (*Soc. chim. Belg.*, 1908, 22, 308—316).—A review of the recent methods proposed, particularly that recommended by Lunge. The author is of opinion that the problem of exact estimation of sulphur has as yet quite solved, especially in the case of zinc ores.

L. DE K.

estimation of Sulphurous Acid in Gelatins and other substances. L. PADÉ (*Ann. Chim. anal.*, 1908, 13, 299—301).—Twenty grams of dry gelatin, or 100 grams of jelly, are placed in a flask containing 500 c.c. of boiled water. The flask is fitted with a cork through which pass the usual inlet and outlet tubes and also a separating funnel containing 25 c.c. of syrupy phosphoric acid. After twelve hours, a current of carbon dioxide is passed; the liquid is heated at 70°, and the sulphur dioxide absorbed in nitrogen bulbs containing iodine solution.

After an hour, the bulb-tube is changed, the phosphoric acid is washed from the funnel, and the operation continued for another hour. In this way, the sulphur dioxide present as sulphites is estimated.

The sulphur dioxide is converted by the iodine into sulphuric acid, which is then estimated gravimetrically.

L. DE K.

Ammonia Distillation in the Presence of Magnesium or Magnesium Salts. PHILIP ADOLPH KOBER (*J. Amer. Chem. Soc.*, 1908, 30, 1281).—The time required for distilling off the ammonia in Folin's method of estimating carbamide (Abstr., 1903, ii, 116) is three or four times greater than that required for ordinary ammonia distillation. Further, the results of such ammonia distillations show considerable variation, especially when made in the presence of magnesium or magnesium salts. These facts are discussed, and an explanation is given.

The solvent action of ammonia or its salts on magnesium hydroxide is due to the following reaction: $MgCl_2 + 2NH_4OH \rightleftharpoons Mg(OH)_2 + 2NH_4Cl$. The liquid from which the ammonia is distilled in Folin's method contains a large excess of magnesium chloride, and some ammonium chloride, magnesium hydroxide, and ammonia. As the concentration of the magnesium hydroxide is extremely small and that of the magnesium chloride relatively great, equilibrium will not occur until most of the ammonia is in the form of ammonium chloride. A small amount of the ammonia is removed by distillation, and the equilibrium is disturbed, so that a further quantity of ammonium hydroxide is formed. This gradual change explains the slowness with which the ammonia passes over in carbamide estimations made with magnesium or magnesium chloride. It has been found very difficult, if not impossible, to distil ammonia from an alkaline saturated solution of magnesium or magnesium chloride. It is therefore evident that quantitative ammonia distillations should not be carried out in the presence of large quantities of magnesium or calcium salts.

E. G.

Electrolytic Estimation of Nitric Acid. OWEN L. SHINN (*J. Amer. Chem. Soc.*, 1908, 30, 1378—1381).—Easton (Abstr., 1904, ii, 116) has studied the reduction of potassium nitrate to ammonia by

electrolysis in presence of copper sulphate. A further investigation was made by Ingham (Abstr., 1905, ii, 61), who, by employing a current density and a rotating anode, obtained very accurate results. As several subsequent workers have been unable to obtain satisfactory results by this method, a series of experiments has been made in order to determine the best conditions. It has been found that high results can be obtained if the anode is rotated slowly so as to prevent the precipitation of the copper. The current should be about 4 amperes and 10 volts, and not more than about 20—25 c.c. of sulphuric acid should be present. It is sometimes necessary to add a second or even a third quantity of copper sulphate in order to complete the reduction.

Detection of Nitrates in Wine and Must. T. MARSHALL *Chem. Zentr.*, 1908, i, 2204; from *Staz. sperim. agrar. ital.*, 1908, 41, 162.—One hundred c.c. of the wine are concentrated in a flask to 10 c.c. and, when cold, 6 c.c. of a saturated solution of ferrous sulphate and 4 c.c. sulphuric acid are added and the liquid slowly boiled. By means of a condenser, the vapour is collected in a suitable vessel containing 2 or 3 c.c. of a specially prepared, acidified starch-potassium solution. When nitrates are present in the wine, a blue ring is produced in the starch solution, either at once or in the second or third small fraction, according to the quantity present.

The starch solution is prepared by shaking starch with water, warming on a water-bath, and adding zinc chloride; after acidifying and allowing to cool, the potassium iodide is added. This method of detecting nitrates is not applicable to must, or wine of a high alcohol content; with such, the following method of Zecchini is adopted. The must is evaporated to dryness with fresh lime on a water-bath and then extracted with 96% alcohol and filtered; the filtrate is evaporated, extracted with water, and then submitted to the method described above for wine.

Detection of Phosphoric Acid in Stones, Ores, and Minerals. ALEXANDER P. LITOFF (*J. Russ. Phys. Chem. Soc.*, 40, 817—822).—The presence of phosphoric acid in minerals is readily detected as follows: The finely powdered mineral is strongly heated in a crucible or iron tube in order to free it from water, organic matter, and carbon dioxide. From 0.5 to 1.0 gram of the cooled mineral is then mixed with approximately 0.5 gram either of magnesium or of a mixture of about 65% of magnesia and 35% of aluminium. The mass is introduced into a test-tube about 5–6 cm. long and 3 mm. in diameter, a loose plug of wool being placed above it. The tube is then heated until the lower part becomes dull red, after which it is rapidly cooled and the contents removed with a thick wire and introduced into a test-tube of spherical enlargement at the upper part. In this test-tube the mixture is gently heated with 20% potassium hydroxide solution, the evolved being passed through a calcium chloride tube and a plug of cotton wool, and over a strip of filter paper moistened with 5% acetate slightly acidified with acetic acid. If phosphorus is present,

filter paper blackens, owing to the formation of copper phosphide, in moist air, gradually becomes decolorised, in consequence of the reaction to colourless copper phosphite.

The dark coloration of the filter paper moistened with copper acetate is determined by arsenic or nitrogen in the mineral. In the case of the hydrogen arsenide sometimes gives a characteristic black arsenic deposit, which is not easily confused with the black, due to the formation of copper phosphide, and which remains unchanged in the air. When nitrogen is present in small proportion, a small amount of ammonia evolved simply forms ammonium, and the colour of the filter paper remains unchanged; when ammonia is evolved, a dark blue solution of copper oxide in water is formed on the filter paper, which changes to the cinnamon of cuprous oxide on heating. Experiment shows that magnesia does not absorb an appreciable proportion of nitrogen at a red heat.

T. H. P.

Determination of Phosphoric Acid in Superphosphates. S. KOHN *Zeit.*, 1908, 32, 718-719.—A slight modification of the process (this vol., ii, 531). Fifty c.c. of the aqueous solution sample are diluted with 300 c.c. of water, and titrated with sodium hydroxide, using a mixture of methyl-orange and indigo indicator. Another 50 c.c. are then mixed with an excess of stannous chloride, and titrated without further dilution, using phenolphthalein as indicator. Salts of iron or aluminium do not interfere.

L. DE K.

Determination of Phosphoric Acid as Phosphomolybdate. P. CHRISTENSEN (*Zeitsch. anal. Chem.*, 1908, 47, 529-545. *Abstr.*, 1907, ii, 652).—The estimation of phosphoric acid by precipitation of the precipitate of ammonium phosphomolybdate was found to be trustworthy for the analysis of soils if carried out in the following manner. A known volume of the extract of the soil (equivalent to about 33 grams of the latter) is evaporated to dryness after the addition of a few drops of nitric acid; the residue is then moistened with dilute nitric acid, again evaporated, and heated to a temperature of 120° for fifteen minutes. The residue is next treated with 100 c.c. of boiling water and a few drops of nitric acid, the silica is filtered on a filter, and washed with water until the filtrate contains about 40 c.c. The filtrate is neutralised by the addition of 10 c.c. of N 0.91, a further 8 c.c. of ammonia are added, and then concentrated nitric acid. The mixture is heated to about 100° when all the precipitated ferric hydroxide has re-dissolved, the acid solution is run in with constant stirring. About 10 c.c. of a 5% ammonium nitrate solution are added for every 0.1 gram of phosphoric oxide. After the lapse of three hours, the precipitate is collected on a filter, washed with a 5% ammonium nitrate solution containing 1% of nitric acid, dried, and ignited at a temperature not exceeding a dull red heat. The filter paper is burnt before adding the precipitate to the dish, and the latter is not covered until the ignition is nearly

completed. The weight of the precipitate multiplied by 0.0394 the quantity of phosphoric oxide. W. P.

Direct Estimation of Phosphoric Acid as Ammonium Phosphomolybdate. EMIL RABEN (*Zeitsch. anal. Chem.*, 1908, 546).—As ammonium nitrate is readily soluble in alcohol, the precipitate of ammonium phosphomolybdate obtained in the usual in the estimation of phosphoric acid may be washed with alcohol weighed. The precipitate is collected on an asbestos filter, washed ammonium nitrate solution, then a few times with warm 70% alcohol with absolute alcohol, and, finally, with a little ether. precipitate is dried to constant weight at a temperature of 110.—

W. P.

Pemberton's Method for the Estimation of Phosphoric Acid. G. H. G. LAGERS (*Zeitsch. anal. Chem.*, 1908, 47, 561—Compare Abstr., 1907, ii, 907).—The method was found to give worthy results if the solution containing the water-soluble phosphoric acid received the addition of at least 58 milligrams of sulphuric acid before the phosphoric acid was precipitated with the molybdate. When smaller quantities of sulphuric acid (compare Abstr., 1907, 419) were added, the results obtained were too low. W. P.

Detection of Traces of Arsenic in Various Substances: the Sensibility of the Usual Methods. C. H. NIEUWLAND (*Weekblad*, 1908, 5, 558—561).—Sjollem's method (this vol., ii, 361) can be applied to the detection of traces of arsenic in milk, wheat-meal, beef-suet, calico, beer, wall-paper, bones, bone-marrow, and yams. The arsenic was introduced by means of a solution of potassium arsenite containing 0.1 milligram of arsenious oxide; Gutzeit's test is more delicate; but with not less than 0.05 milligram of arsenious oxide, Sjollem's method enables arsenic to be distinguished from antimony and phosphorus. A. J.

Detection of Boric Acid in Foods by means of Turmeric Paper. FRANCISCO P. LAVALLE (*Chem. Zeit.*, 1908, 32, 816—817).—In order to render turmeric paper more delicate, it has been recommended to extract the turmeric powder with benzene before preparing the tincture. The author states that a reaction for boric acid obtained by means of this paper must on no account be taken as proving a wilful addition of boric acid; the reaction is too delicate, showing the (apparent) presence of boric acid even in such reagents as pure hydrochloric acid, sodium chloride, &c. L. DE

The Estimation of Graphite. FRANK BROWSE (*Chem. Zeit.*, 1908, 32, 51).—The author has studied the influence of heat on the conversion of ferric oxide into the magnetic oxide, and, as a result, has devised the following process for the estimation of graphite: ferric oxide is heated to redness in a covered crucible for two to three hours; the resulting oxide is a nearly black, slightly coherent mass of powder. About 5 grams of this oxide are heated in an annealing furnace at 1000° C. for 24 hours. The resulting oxide is a

mouthed crucible at a pale red heat for an hour, with occasional weighing; after weighing, 0.5 gram of graphite is added and heated as before for one or two hours, with occasional stirring, again weighing. The carbon is burnt off, and the oxide remains unchanged. The results agree fairly closely with those obtained by the potash fusion method. The mineral matter of coal may be estimated in the same way, but the amount found will be about 0.5 per cent. higher than that estimated in the ordinary manner, owing, probably, to interference of the constituents of the ash.

P. H.

Determination of Potassium in Silicates. WILHELM AUTENRIETH *et Min.*, 1908, 513—517).—The mineral is decomposed by heating with hydrofluoric and sulphuric acids. When dry, the mass is extracted with boiling water, and the solution freed from iron, etc., by boiling with excess of sodium acetate. After concentrating to 10 c.c., the potassium is precipitated as cobalt-yellow by addition of 10 c.c. of de Koninck's cobalt reagent. As, however, the silicate is not of constant composition, it is dissolved in hydrochloric acid, and the residue left on evaporation is treated for sodium by the well-known perchlorate method. The potassium may be estimated also by the usual platonic chloride method; in this the cobalt must be eliminated by gently igniting the precipitate and extracting the mass with hot water.

The cobalt reagent is prepared by dissolving 30 grams of crystallised potassium nitrate in 60 c.c. of water, adding 100 c.c. of a saturated solution of sodium nitrite, and then 10 c.c. of glacial acetic acid. In a few days, the reagent is poured off from any deposit, and is fit for use; it keeps, in the dark, for about a month.

L. DE K.

Determination of the Alkaline Earths [in Waters] by means of Potassium Stearate and Phenolphthalein. C. BLACHER and POLY (*Chem. Zeit.*, 1908, 32, 744—745).—The carbonates are titrated with *N* 10 hydrochloric acid, using methyl-orange as indicator, and the carbon dioxide is removed by a current of air. Diphtalatin and a few drops of alcoholic *N* alkali are added, and the solution decolorised with *N* 10 hydrochloric acid. After adding an 0.02 c.c. of acid, the total hardness is determined by titrating with *N* 10 potassium stearate until the liquid turns red. The calcium is estimated in the presence of magnesium by placing 200 c.c. of water in a flask and weighing the same. After neutralising with *N* 10 hydrochloric acid, the carbon dioxide is boiled off, 1—3 c.c. of alcoholic alkali is added, and the loss in weight restored by adding water free from carbon dioxide. The liquid is filtered while hot, and, when cold, 100 c.c. are neutralised as directed, and calcium is titrated with the stearate solution. Sulphates may be determined indirectly by precipitating with a slight excess of barium chloride and determining the excess with the stearate solution, allowing made for any calcium and magnesium present.

The reagent is prepared by dissolving 28.4 grams of stearic acid in 100 c.c. of hot alcohol and 2.0 grams of glycerol, and neutralising

with alcoholic potassium hydroxide. When cold, the whole is dil. with alcohol to one litre. If desired, the solution may be dil. with lime-water and $N/10$ acid. L. DE

Volhard's Copper Titration. H. THEODOR (*Chem. Zeit.*, 1908, 32, 889—890).—Volhard's process (precipitation of copper in presence of sulphurous acid with ammonium thiocyanate and estimation of excess of the latter with silver solution) is strongly recommended. L. DE

Analysis of Bronzes, Brass, and Similar Alloys. SCHÜRMANN and H. ARNOLD (*Chem. Zeit.*, 1908, 32, 886—887).—A solution of the alloy, which should contain, besides tartaric acid, about 5% of free nitric acid, is submitted to electrolysis; condition: 10 amperes and 4 volts. This precipitates the copper only (tin, however, should be examined for traces of tin), whilst antimony and tin remain in solution. After rendering alkaline with potassium hydroxide, lead and any copper still present are precipitated by cautious addition of potassium sulphide, and then treated by the usual methods. The filtrate is boiled with addition of 0.5 c.c. of hydrogen peroxide, and, after neutralising with oxalic acid, an excess solution of 5 grams of that acid is added. The liquid is then to 400 c.c., heated to boiling, and treated with hydrogen sulphide to precipitate the antimony, which is then collected, dissolved in sodium sulphide, and submitted to electrolysis. The filtrate of antimony is neutralised with ammonia, acidified with acetic acid, heated to boiling, and treated with hydrogen sulphide. The tin sulphide is then converted as usual into tin oxide.

A number of test-analyses are given.

The process is also applicable to the analysis of brass. At first, copper has been separated electrolytically, the liquid is then treated with hydrogen sulphide, and the precipitate submitted to the usual methods. The filtrate containing the zinc is then analysed for zinc by the ordinary way. L. DE

Estimation of Manganese in Iron and Manganese Ores. MAX ORTNEY (*Zeitsch. anal. Chem.*, 1908, 47, 547—560).—Results of a critical examination of some of the methods for the estimation of manganese are given, particular attention being paid to the more rapid volumetric processes. For the estimation of manganese in iron and manganese ores, the methods proposed by Volhard-Wolf, von Kuorle (Abstr., 1902, ii, 108), and Böhm (Abstr., 1904, ii, 683), were found to be trustworthy, the results agreeing well with those yielded by the ordinary gravimetric method. W.

Direct Combustion of Steel for Carbon and Sulphur. HELEN ISHAM and JOSEPH AUMER (*J. Amer. Chem. Soc.*, 1908, 30, 1236—1239).—Experiments showing that the carbon in steel is almost completely eliminated by direct ignition in a current of oxygen.

en, whereas the sulphur cannot be expelled completely in this way.

The results for carbon average 0.004% more than those obtained by the usual copper chloride method.

L. DE K.

Loss of Carbon during Solution of Steel in Potassium Cupric Chloride. ERNEST P. MOORE and JAS. VASSON BAIN (*J. Soc. Chem. Ind.*, 1908, 27, 845—846).—In order to ascertain whether there was any loss of carbon when steel is dissolved in potassium cupric chloride solution, the authors carried out experiments in which the loss of steel were dissolved in the solution in a flask through which a current of air free from carbon dioxide was passed. After leaving the flask, the air was passed over heated cupric oxide, and then through a barium hydroxide solution. The barium carbonate formed was collected and estimated. From the results obtained, it is found that the loss of carbon from 1 gram of steel amounted to 0.0004 to 0.0005 gram. The two samples of steel used in the experiments contained 0.653 and 1.18% of carbon respectively.

W. P. A.

Pure Ferric Oxide as a Standard Substance for the Estimation of Iron in Hydrochloric Acid Solution. L. BRANDT (*Chem. Zeit.*, 1908, 32, 812—814, 830—832, 840—843, 851—853).—A lengthy article, unsuitable for adequate abstraction. The chief point is the preparation of a pure oxide of iron, which may then be dissolved in hydrochloric acid, and serve for the standardising of permanganate after the usual reduction with stannous chloride.

50 grams of a commercially-pure iron free from zinc are dissolved in hydrochloric acid, and a current of hydrogen sulphide is passed through the solution. The filtrate is boiled, and oxidised with nitric acid. The filtrate is concentrated, and evaporated twice with hydrochloric acid. The residue is dissolved in hydrochloric acid, D. 1.104, and shaken with ether in a separating funnel with ether, which dissolves the ferric chloride. Should the iron contain cobalt, this will also pass into the ether, but may be removed by shaking the ether with 10% solution of hydrochloric acid, D. 1.104, saturated with ether. The ether is evaporated, and the residual ferric chloride converted to ferric nitrate by repeated evaporation with excess of nitric acid, and with addition of ammonium nitrate. The dry mass is now heated in a platinum dish, finally with addition of ammonium nitrate, until the weight is constant to about 0.01 gram.

L. DE K.

Detection and Estimation of Nickel and Cobalt. M. FERNANDEZ (*Chem. Zeit.*, 1908, 32, 804). A reply to Grossmann (*ibid.*, ii, 230). The author upholds the accuracy of his own process.

L. DE K.

Ammonium Molybdate as a Reagent for Nickel. HERMANN VON BERNARD SCHUCK (*Bull. Soc. chim.*, 1908, [iv], 3, 884). In this vol., ii, 230. A reply to Pozzi-Escot (this vol., ii,

F. A. H.

Detection of Chromium. M. EMMANUEL POZZI-ESCOR (*Ann. chim.*, 1908, 13, 333).—The solution, which, besides chromium, contains a large excess of iron, manganese, cobalt, nickel, copper, &c., heated to boiling, a solution of sodium hypobromite containing an excess of alkali is added, and the boiling is continued for 5 minutes. When cold, the solution is filtered, and the chromate is identified by the usual tests, such as lead acetate and acetic acid.
L. DE

Estimation of Chromium and Tungsten in Steel. F. V. HINRICHSSEN and LUDWIG WOLTER (*Zeitsch. anorg. Chem.*, 1908, 183–197).—Attempts were made to separate tungsten and chromium by precipitating the former as tungstic acid with nitric acid, but precipitation was incomplete. On the other hand, reduction of chromate to chromic salt and precipitation with ammonia gave poor results. Good results were finally obtained by precipitating tungsten (and a small part of the chromium) with benzidine hydrochloride according to Knorre (*Abstr.*, 1905, ii, 286), the amount of chromium in the precipitate being determined by oxidising chromate and estimating with potassium iodide and thio-sulphate the usual way. With certain precautions, the presence of tungstic acid does not interfere with the iodometric estimation of chromium.

In the presence of chromium, the results for tungsten obtained by the benzidine method are somewhat too low, and this point is under investigation.

On the other hand, satisfactory results for both metals were obtained by precipitating both chromium and tungsten from any part of the solution by means of mercurous nitrate (benzidine method), estimating the chromium in another portion of the solution by the iodometric method. The precipitation is done as follows: To 10 cc. of the solution containing chromate and tungstate, heated to boiling, a saturated solution of mercurous nitrate is added, and the ammonia added drop by drop until the precipitate becomes dark. The mixture is then boiled, filtered, dried, ignited, and the residue weighed.

Estimation of Vanadium, Molybdenum, Chromium, and Nickel in Steel. ANDREW A. BLAIR (*J. Amer. Chem. Soc.*, li, 1229–1235).—Two grams of the sample are converted into ferric chloride, which is then dissolved in a little hydrochloric acid. The solution is shaken first with SO_2 and then again with ether, which dissolves the iron and also the molybdenum. It is then shaken with water, and the aqueous solution evaporated to excess of sulphuric acid. The ferric sulphate is then dissolved in water, and reduced by boiling with ammonium hydrogen sulphide. The molybdenum is precipitated by means of a current of hydrogen sulphide, collected in a Gooch crucible, and converted to molybdenum trioxide by cautious ignition. As it always contains a little iron, it is dissolved off the filter by means of dilute ammonia, and the iron is weighed.

The liquid which has been extracted with ether is re-

aporated with nitric acid to a syrupy condition, dissolved in 20 c.c. of hot water, and, after reducing any chromate formed by means of sulphurous acid, poured into a boiling 10% solution of sodium hydroxide. The precipitate contains the oxides of chromium and manganese, also the bulk of the manganese, and traces of iron and copper. The filtrate, which contains the vanadium and sometimes a trace of chromium, besides any silica and alumina, is acidified faintly with sulphuric acid, and then again rendered slightly alkaline and boiled to remove the last traces of chromium. To the filtrate are added 10 c.c. of 10% lead nitrate and then a little acetic acid, and, after standing for a few minutes, the lead vanadate is collected and evaporated to dryness. A large excess of hydrochloric acid to effect reduction. The hydrochloric acid is then completely expelled by evaporation with excess of sulphuric acid, and the residue, after being diluted to 150 c.c., is treated for vanadium at 60—70° with standard permanganate. The filtrates containing the two precipitates from the soda solution are filtered, and the ash fused with 2 grams of sodium carbonate and 1 gram of potassium nitrate. The mass is then extracted with water. The insoluble portion contains nickel, copper, iron, and part of the manganese. It is dissolved in hydrochloric acid, the copper is precipitated by hydrogen sulphide, and the filtrate evaporated with excess of sulphuric acid. The residue is diluted with water, excess of potassium permanganate is added, and the nickel deposited electrolytically. The filtrate, which contains the chromium and the remainder of the manganese, is mixed with excess of ammonium nitrate and evaporated to dryness; addition of ammonia; this precipitates the manganese, also any iron and alumina. The filtrate is then boiled, reduced with sulphurous acid, and the chromium precipitated by ammonia and weighed as oxide.

L. DE K.

Determination of Vanadium in Iron and Steel. EDWARD DE MILLE and EDWIN LEGRAND WOODHAMS (*J. Amer. Chem. Soc.*, 30, 1233—1236).—Five grams of the sample are dissolved in concentrated sulphuric acid, and the insoluble matter, which contains part of the vanadium, is collected and burnt, and finally treated with hydrofluoric acid to expel silica. The soluble portion is treated with hydrogen sulphide to precipitate the iron, and the filtrate evaporated to about 35 c.c., and the greater portion of the ferrous sulphate precipitated by addition of 100 c.c. of alcohol. The filtrate is acidified with hydrogen peroxide, boiled, and precipitated with sodium carbonate. The precipitate is collected, and to it is added the residue from the first step of the analysis. The whole is fused with sodium carbonate, and then 300—400 milligrams of charcoal are added and the fusion continued for ten minutes in the covered crucible. The object of the charcoal is to reduce any chromate formed; sodium vanadate is collected.

The mass is now extracted with hot water, 10 c.c. of sulphuric acid (1:1), are added, and then 3—4 c.c. of 3% potassium permanganate. After boiling for five minutes, sulphurous acid is added until the permanganate has been reduced and the vanadic acid precipitated into the blue divanadyl sulphate. The solution is then evaporated until sulphuric fumes appear, and, when cold, water is added up to

60 c.c. and the warm liquid titrated with $N/20$ permanganate, 1 c.c. which = 0.00256 gram of vanadium. L. DE K.

Estimation of Alcohol in Fermented Liquids. WM. ANI (*J. Amer. Chem. Soc.*, 1908, 30, 1276—1278).—The wine or other alcoholic liquid is introduced into a specially constructed pycnometer of the Sprengel type, brought to the required temperature by immersion in a bath, and weighed. By means of a rinsing arrangement, the wine is introduced into the distilling flask, and the distillate is collected in pycnometer, which is then carefully filled up with water and weighed. For details, the original paper and illustrations should be consulted. L. DE K.

Detection of Formaldehyde. FRANZ VON FILLINGER (*Zeit. Nahr. Genussm.*, 1908, 16, 226—231).—The paper is written with object of drawing general attention to the usefulness of the method described by Hehner for the detection of formaldehyde. The author discusses the chemistry of the reaction (compare Abstr., 1907, ii, 512), and gives general directions for its application. W. P.

The Value of the Different Methods Used for Estimating Sugar in Urine. CASIMIR FUSK (*Zeitsch. physiol. Chem.*, 1908, 507—511).—Bertrand's method for estimating sugars (Abstr., 1907, ii, 136) gives very good results for mines, except when β -hydroxybutyric acid is present.

Bang's method gives good results with pure sugar solutions, but with urines. Borchardt's suggestion, that diabetic urine contains an unknown levorotatory sugar, is not accepted. J. J. S.

Estimation of Reducing Sugars. FRITZ ZERBAN and W. NAQTIN (*J. Amer. Chem. Soc.*, 1908, 30, 1456—1461).—The cuprous oxide formed by the action of the reducing sugar on Fehling's solution is collected in a Munro-Neubauer crucible, and the precipitate converted into copper oxide by heating for ten minutes over a Bunsen flame.

In some cases there may be present co-precipitated mineral matter; the real amount of copper oxide must then be estimated by accurate method, such as Low's volumetric process.

Some sugars contain reducing substances other than sugar; in such cases, clarification with normal lead acetate is resorted to, which will partly remove such matters. L. DE K.

Detection and Identification of Certain Reducing Sugars by Condensation with *p*-Bromobenzylhydrazide. E. C. KIRBY and HENRY C. SHERMAN (*J. Amer. Chem. Soc.*, 1908, 30, 1451).—The reagent is prepared by heating on a water bath a mixture of 10 grams of ethyl *p*-bromobenzoate, 8.2 grams of a 50% aqueous solution of hydrazine hydrate, and 12 c.c. of 95% alcohol. After 48 hours, the alcohol is distilled off, and the residue, after being washed with ether, is recrystallised from alcohol.

The test is applied by heating about 0.03 gram of the sugar

* and *Full. Assoc. chem. Soc. Dist.*, 1908, 26, 177—182.

its weight of the reagent in presence of alcohol. After evaporating three or four times with alcohol, the residue is boiled in chloroform and a few drops of water, which leaves the condensation product undissolved. The reaction is obtained with dextrose, lactose, mannose, and arabinose; not with levulose, maltose, or sucrose, and only to a slight extent with xylose.

The *p*-bromobenzylhydrazono of galactose is insoluble in boiling alcohol, those of mannose and arabinose are dissolved partly, whilst that of dextrose is completely dissolved. The non-reacting sugars, however, interfere with the formation of the dextroso hydrazone to an extent comparable with the interference of maltose and lactose in the osazone reaction for dextrose.

L. DE K.

Test for Pentoses with Orcinol and Hydrochloric Acid. PIERAERTS (*Bull. Assoc. chim. Sac. Dist.*, 1908, 26, 46—52).—Sugars with a keto-group, such as levulose, produce colorations with orcinol and hydrochloric acid which obscure the colour given by pentoses; hence levulose and its anhydrides should first be eliminated by fermentation with yeast. In employing the orcinol reagent of Fieser, it is advisable to add an additional volume of concentrated hydrochloric acid to the mixture of one volume of the reagent with one volume of the pentose solution.

G. B.

Formic Acid in Glacial Acetic Acid. H. OST and F. KLEIN (*Monatsh. Zeit.*, 1908, 32, 815—816).—Wegener's process for formates is recommended. Ten c.c. of the sample are heated with 50 c.c. of sulfuric acid in a flask from which the air has been expelled by a current of carbon dioxide. The mixture is heated on the water-bath for one hour, and the gas evolved collected, with the usual precautions, in aqueous potassium hydroxide; 100 c.c. of carbon monoxide = 0.66 gram of formic acid.

Good results are also obtainable in the case of weaker acids with potassium permanganate or Macnair's dichromate process, or with the mercuric chloride reduction method.

L. DE K.

Estimation of the Acidity of Wines. G. FAVREL (*Ann. Chim.*, 1908, 13, 315—316).—Three official methods are in use. (1) Titration with sodium hydroxide, using phenolphthalein as indicator; (2) Titration with lime water until a flocculent precipitate forms. The author states that there is a discrepancy between the results obtained by the first and the second methods, and expresses the hope that analysts will adopt the first method.

L. DE K.

Direct Estimation of the Acidity of Wines. G. FAVREL (*Chim. anal.*, 1908, 13, 343—346).—Ten c.c. of the wine free from carbon dioxide are placed in a separating funnel, and 20 c.c. of sodium hydroxide free from carbonate are added. A quantity of benzoic acid, known from a previous experiment to neutralise exactly the wine, is introduced, and the whole is well shaken. The liquid now contains free benzoic acid equivalent to the acidity of the

wine, is shaken twice in succession with 40 c.c. of ether, and the liquid is slowly distilled until about 20 c.c. are left. The residue is allowed to evaporate in a beaker, and the flask is rinsed first with 10 c.c. of water and then with 5 c.c. of alcohol, which is poured into the beaker. The alcoholic solution is then titrated with $N/20$ sodium hydroxide solution using phenolphthalein as indicator. L. DE K.

New Method of Estimating the Fixed and Volatile Acids in Wine. M. EMMANUEL POZZI-ESCOR (*Compt. rend.*, 1908, 1, 245—247; *Bull. Soc. chim. Belg.*, 1908, 22, 338—340; *Bull. chim. Soc. Dist.*, 1908, 23, 68—69).—The method is based on transformation of the barium salts of the fixed acids into carbonates by suitable heating and titration of these by standard acid. Two samples each of 100 c.c. are concentrated to 3—4 c.c. in flat porcelain capsules. The product of the first is treated with an excess of alcohol, filtered, and the filter calcined in a muffle furnace. The alkalinity of the filtrate is determined by titration with standard nitric acid, using methyl orange as indicator. The second sample, after evaporation, is neutralized with baryta, and treated with 100 c.c. of a 2% solution of barium chloride in alcohol (96%). The barium salts of the fixed organic acids (except lactic acid) are precipitated immediately and completely; the volatile acids are soluble. The precipitate is filtered off, washed with strong alcohol (in which the barium salts of the volatile acids are soluble), drained, and calcined in a porcelain crucible in a muffle furnace. The carbonates formed are titrated with standard nitric acid, and the result, after deduction of the acidity obtained from the first experiment, corresponds with the acidity due to the fixed acids. Subtraction of the acidity due to the fixed acids from the total acidity of the wine, determined on 100 c.c. using phenolphthalein as indicator, gives the acidity due to volatile acids. The author claims that the method is rapid and simple. It is only applicable to the estimation of organic acids, and is inexact in the presence of lactic acid, but the presence of the latter in wine is quite exceptional. E.

The Natural Citric Acid of Wine. E. DUCROT (*Ann. Chem. anal.*, 1908, 13, 338—343).—A study of the Denigès mercury reaction for citric acid. Most wines from the South of France give a reaction, but, unless they are preserved by means of sulphur dioxide, the acid disappears within a few months. The author thinks the reaction may be made approximately quantitative. As comparison liquid should be used a wine itself free from citric acid, but to which a known quantity of the acid has been added. L. DEL.

Estimation of Malic Acid in Food Products. H. W. COWIE (*J. Amer. Chem. Soc.*, 1908, 30, 1285—1288).—The process is described for the estimation of malic acid in maple products, but may be applied to other products, such as cider, cider vinegar, etc.

6.7 Grams of the sugar or syrup are dissolved in 5 c.c. of water. 2 c.c. of 10% calcium acetate are added, followed by 100 c.c. of 95% alcohol, and the whole is warmed on the water-bath until the precipitate has settled completely. The precipitate is washed free from sugar

ers with 85% alcohol and then burnt to carbonate. This is then treated as usual by dissolving in *N*/10 hydrochloric acid and titrating back with *N*/10 sodium hydroxide. The alkalinity represents malic acid. L. DE K.

Estimation of Tartaric Acid in the Presence of Malic and Citric Acids. L. GOWING-SPODES (*Analyst*, 1908, 33, 315—319).—The author has submitted the method proposed by Ferentzy (Abstr., 1907, ii, 931) to a critical examination, and finds that it is trustworthy. He stated, however, that more accurate results may be obtained by titrating the magnesium basic tartrate with potassium permanganate by igniting it as recommended by Ferentzy. The method may be applied to the estimation of tartaric acid in fruit juices, and in wines if the malic acid is first removed. W. P. S.

Estimation of Lactic Acid; Comparison of Methods. JOSEF MUMER (*Chem. Zentr.*, 1908, ii, 101; from *Zeitsch. landw. Versuchs. Oesterr.*, 1908, 11, 492—505. Compare Abstr., 1903, ii, 189).—The method of Kunz (Abstr., 1901, ii, 790), with some slight modification, is applicable in all cases for the estimation of lactic acid, and gives more trustworthy results than does the method of Jinger (Abstr., 1902, ii, 181). J. V. E.

A New Process for the Estimation of Lactic Acid in Organic and Animal Fluids. I. Estimation of Lactic Acid in Aqueous Solutions. ERNST JERUSALEM (*Biochem. Zeitsch.*, 1908, 12, 379—378).—The lactic acid is estimated by oxidising to acetaldehyde: $\text{CH(OH)CO}_2\text{H} + \text{O} = \text{CH}_3\text{CHO} + \text{CO}_2 + \text{H}_2\text{O}$, and estimating the aldehyde thus formed by treating with excess of iodine in alkaline solution, and afterwards estimating the excess not used for the formation of iodoform from the aldehyde. To get trustworthy results, the oxidation must be carried out by warming the liquid containing the lactic acid with sulphuric acid, and adding permanganate solution to the boiling mixture. The aldehyde as it is formed must be removed quickly as possible from the boiling liquid; this is accomplished by means of a current of air. The apparatus for the absorption of the aldehyde must also be very efficient, and one, specially devised, is figured in the original paper. In animal tissues, other substances are found which will interfere with the accuracy of the determinations, especially the sugars and acetone. Tissues must therefore be evaporated down and extracted with ether, and the lactic acid estimated in the ethereal extract. S. B. S.

A New Process for the Estimation of Lactic Acid in Organic and Animal Fluids. II. Estimation of Lactic Acid in Animal Fluids. ERNST JERUSALEM (*Biochem. Zeitsch.*, 1908, 12, 379—389).—For estimating the lactic acid in animal tissues and liquids, the acid must be first extracted with ether (see preceding abstract). Quantitative extraction can only be accomplished when the liquid to be treated is so concentrated as to be of pasty consistency. A special apparatus for the extraction of such liquids is figured and described in

the paper, and also the application of the method to special cases, as the estimation of lactic acid in blood, milk, urine, &c. S. B. S.

Detection and Estimation of Boric Acid, Salicylic Acid, Benzoic Acid in Foods, etc. WILHELM VON GENESEICH (*Zell. Nahr. Genussm.*, 1908, 16, 209—225).—The results of a critical examination of many of the methods proposed for the detection and estimation of these acids are given. Amongst others, the method described by Windisch (*Abstr.*, 1905, ii, 554) was found to be trustworthy for the estimation of boric acid, as was also Freyer's volumetric process for estimating salicylic acid. Benzoic acid is best extracted from food materials by means of benzene, or mixtures of the latter with light petroleum. The benzene solution of the acid may be evaporated after the addition of ammonia, or a portion of it may be titrated with standard alkali solution. W. P. S.

Detection of Benzoic Acid in Butter. (GEORGES HALL (*J. Pharm. Chim.*, 1908, [vi], 28, 201—203 *))—The test proposed is a modification of that described originally by Möller, in which benzoic acid is converted into ammonium diaminobenzoate; this, when treated with alkalis, gives a brownish-red coloration. Butter to be tested is melted, together with sufficient lime-water to render the aqueous portion distinctly alkaline; after cooling, the aqueous portion is separated, rendered acid with phosphoric acid, shaken out with ether. The ethereal extract is evaporated at ordinary temperature, and the dry residue is dissolved in 2 c.c. sulphuric acid, the mixture being heated slightly to dissolve benzoic acid. When cold, 0.2 c.c. of fuming nitric acid is added, the solution is transferred to a test-tube, and heated, with constant agitation, over a small flame until it boils. The heating is continued, without agitating the contents of the tube, until sulphuric acid vapours commence to be evolved. After cooling, 6 c.c. of water are added, and then saturated sodium sulphite solution, drop by drop, until all the yellow vapours have disappeared. Ammonia is then allowed to flow over the surface of the liquid, when, if benzoic acid is present, an orange-red coloration is obtained, the intensity of which depends on the quantity of benzoic acid in the sample. W. P. S.

Separation and Estimation of Salicylic Acid and Methyl Salicylate: Hydrolysis of Methyl Salicylate. H. D. G. (*J. Amer. Chem. Soc.*, 1908, 30, 1465—1470).—*Estimation of Methyl Salicylic Acid in Oil of Gaultheria*.—Five to twenty c.c. of these oils are shaken with an equal volume of water, and titrated with 0.1 N sodium hydrogen carbonate, using Congo-red as indicator.

Preparation and Estimation of Salicylic Acid and Methyl Salicylate in Foods and Drugs.—The substance is extracted with 10% sodium hydrogen carbonate, which dissolves the salicylic acid and a portion of the ester; the remaining ester is recovered by acidifying with dilute sulphuric acid, and distilling in a current of steam; the ester is then shaken out with chloroform. The filtrate is shaken with chloroform to remove the dissolved ester, and the salicylic acid

* *Anal. Ann. Chim. anal.*, 1908, 13, 382—384.

covered from the alkaline solution by acidifying and shaking with chloroform; finally, the acid is determined colorimetrically.

The chloroform extracts containing the ester are boiled in a reflux apparatus with excess of potassium hydroxide, and the salicylic acid formed is then estimated as directed.

For the methods of studying the rate of saponification of the ester with sodium hydroxide and carbonate, the original article and curves should be consulted. Methyl salicylate, on keeping, always becomes slightly hydrolysed.

L. DE K.

Characteristic Test for Hippuric Acid [in Urine]. WILLIAM DEHN (*J. Amer. Chem. Soc.*, 1908, 30, 1507—1508).—A few c.c. of the urine are treated in a test-tube with sodium hypobromite just sufficient to decompose the carbamide and impart a permanent, yellow colour. The solution is then heated to boiling, when, should hippuric acid be present, an orange or brownish-red precipitate is formed, which, however, consists partly of earthy phosphates.

The nature of the red precipitate, which contains nitrogen and ammonia, has not yet been fully investigated. It is soluble in most of the organic solvents and in carbon disulphide.

L. DE K.

Apparatus for Estimating the Expansion of Oils and Other Liquids which Boil above 100°. WILHELM THÖRNER (*Chem. Zentr.*, 1908, i, 2001—2003; from *Zeitsch. chem. Apparatenkunde*, 1908, 1, 165—168).—The estimation of the expansion of oils and fats between 0° and 100° is advised as an additional means of identification. A Jena glass flask, having a long neck, which is graduated 1/10 c.c. from the top downwards, and having a capacity of exactly 100 c.c. of distilled water at 100°, is nearly filled with the oil to be tested. The flask is then heated in a suitably arranged steam jacket to 100°, when the volume is made up exactly to the zero mark. The flask and contents are then placed in an ice-chest to cool down to 0°, when the difference in volume may be observed on the graduated neck of the flask. A table of results obtained with thirty-three substances is given, and it is shown that by this method the amount of acetic acid in water solutions may be estimated with a fair degree of accuracy.

J. V. E.

A New Reaction for Distinguishing between Heated and Unheated Milk, and for the Detection of Hydrogen Peroxide in Milk. W. PERCY WILKINSON and ERNEST R. C. PETERS (*Zeitsch. chem. Genusssm.*, 1908, 16, 172—175).—The test is similar to the well-known *p*-phenylenediamine test, but benzidine is used in place of the latter. Ten c.c. of the milk to be tested are treated with 2 c.c. of a 1% alcoholic benzidine solution, from two to three drops of acetic acid, and 2 c.c. of a 3% hydrogen peroxide solution. With unheated milk, blue coloration appears at once, whilst if the milk has been heated to a temperature of, or exceeding, 78°, no change in colour takes place. The test is stated to be more sensitive than the *p*-phenylenediamine reaction, and may be used, conversely, for the detection of hydrogen peroxide.

W. P. S.

Detection of Small Quantities of Turpentine in Lemon Oil. E. M. CHACE (*J. Amer. Chem. Soc.*, 1908, 30, 1475—1477). Fifty c.c. of the sample are distilled in a Ladenburg 3-bulb flask. The first 5 c.c. of the distillate are mixed with an equal volume of glacial acetic acid and cooled in a freezing mixture, 5 c.c. of ethyl nitrite are added, and, after mixing, 2 c.c. of strong hydrochloric acid are added drop by drop. After fifteen minutes, the deposit is collected on a Büchner funnel, using filter-paper under vacuum. The crystals are washed with about 50 c.c. of 95 (vol. %) alcohol, and the filtrate is replaced by the freezing mixture in order to obtain a second crop of crystals; by passing the liquid through the same filter, the crystals are washed with strong alcohol and dried.

The crystals are now dissolved in a small quantity of chloroform and hot methyl alcohol is added until crystallisation sets in, when the liquid is cooled. More methyl alcohol is then added, and the crystals are collected. For microscopical examination, they may be mounted in olive oil. Turpentine yields very characteristic crystals.

L. DEB.

Some Reactions of Terpin. E. ISNARD (*Ann. Chim. anal.*, 1913, 333—334).—*Action of Reagents on Crystallised Terpin.*—Moist on a watch-glass with sulphuric acid, a coloration varying from cherry yellow to salmon-rose is developed. At the same time, the terpin dissolves and emits a characteristic, aromatic resinous odour. Adding a 10% solution of sodium hydroxide, the colour disappears, but the odour becomes still more pronounced. Syrupy phosphoric acid behaves similarly, but no coloration is noticed until heat is applied. If terpin is dissolved in sulphuric acid and then acted on with nitric acid, a yellow coloration is observed, with formation of brown streaks; the solution then becomes colourless and resinified. If nitric acid is added first, the terpin dissolves to a colourless solution, but if now a drop of sulphuric acid is put on the centre, a red spot is formed surrounded by a salmon-rose zone. Terpin shows reducing properties, reducing molybdic and chromic acids in presence of sulphuric acid, and alcoholic solution of ferric chloride and potassium ferricyanide.

Action of Reagents on the Alcoholic Solution of Terpin.—Sulphuric acid turns salmon-rose, whilst the alcoholic solution remains colourless. The coloration disappears on shaking, unless the solutions are concentrated. With a solution containing 200 c.c. of 15% ammonium molybdate, 10 c.c. of sulphuric acid, and 30 c.c. of nitric acid, a coloration is obtained, which takes a long time to develop. After about an hour, it becomes indigo-blue, and after twenty-four hours has changed to bluish-green. The colouring matter is soluble in chloroform. A white deposit is also formed, but this is probably ammonium molybdate precipitated by the alcohol. When heat is applied, the coloration is developed more rapidly, but soon fades. In this case, the characteristic odour is also noticed.

L. DEB.

